

SYNTHESIS AND REACTIVITY OF
ORGANOSULFUR IRON COMPLEXES

by

Gary Bernard Womack
B.S., University of North Carolina
Greensboro, North Carolina

Submitted to the Department of Chemistry
in partial fulfillment
of the requirements for the
degree of
Doctor of Philosophy

at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
September 1984

© Massachusetts Institute of Technology 1984

Signature of Author

Department of Chemistry

Certified by

Thesis Supervisor

Accepted by

Dietmar Seyferth, Chairman,
Departmental Committee on Graduate Students

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY

SEP 14 1984

ARCHIVES

LIBRARIES

This doctoral thesis has been examined by a Committee
of the Department of Chemistry as follows:

Professor Richard R. Schrock _____
Chairman

Professor Dietmar Seyferth _____
Thesis Supervisor

Professor Alan Davison _____

This Thesis is Dedicated
with Love to
my wife, Cathie,
and to my Parents.

SYNTHESIS AND REACTIVITY OF
ORGANOSULFUR IRON COMPLEXES

by

Gary Bernard Womack

Submitted to the Department of Chemistry in September 1984
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy.

ABSTRACT

Chapter 1. "Addition of Alkynyllithium Reagents to (μ -Dithio)-
bis(tricarbonyliron)"

Alkynyllithium reagents attack (μ -S₂)Fe₂(CO)₆ at the sulfur-sulfur bond cleaving it to form (μ -RC \equiv CS)(μ -LiS)Fe₂(CO)₆. Alkylation and acylation of this anion occurs at sulfur to form the (μ -RC \equiv CS)(μ -RS)Fe₂(CO)₆ type complexes. However, protonation or metallation with the Group IVA trialkyl- or triaryl-metal halides yields dithiolene complexes. The formation of these products has been explained in terms of an equilibrium between the sulfur-centered anion species and carbanion species resulting from intramolecular thiolate addition to the α and/or β carbon atom of the RC \equiv C- group. Thus aldehydes were found to react forming dithiolene complexes by addition of the carbonion intermediates to the carbonyl function. Reaction between the PhC \equiv CLi/(μ -S₂)Fe₂(CO)₆ system and methylmercuric chloride gave both the sulfur- and carbon-metallated products depending on the reaction conditions.

Chapter 2. "The Reactivity of (Di- μ -thiol)bis(tricarbonyliron)
Toward Electrophilic Alkenes and Alkynes"

The piperidine induced additions of the thiol functions of (μ -HS)₂Fe₂(CO)₆ to various electrophilic alkenes and alkynes has been studied. With olefins conjugated to a carbonyl group in which there is only one alkyl substituent on the β -carbon, Michael type additions of the thiol ligands to the C=C bands occur to form 2:1 adducts. If two alkyl substituents are attached to the β -carbon, a 1:1 adduct can be isolated in which addition to both the C=C and C=O bond has occurred. These products contain

a three-carbon bridge between the two sulfur atoms and a hemi-thioketal function. Two consecutive thiol additions to electrophilic acetylenes was found to yield complexes with one- or two-carbon bridges between the two sulfur atoms. NMR data was used to determine the type of addition adduct formed as well as an X-ray diffraction study of a one-carbon bridged product.

Chapter 3. "Diiron Hexacarbonyl Complexes of Thioesters and Dithioesters"

The deprotonation of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ with lithium diisopropylamide at -78°C in THF generates an organolithium reagent which undergoes intramolecular nucleophilic attack at iron with concomitant Fe-S bond heterolysis. The sulfur-centered anion species thus generated can be trapped with alkyl halides. An X-ray diffraction study of the 1-bromo-2-propanone derived product reveals these compounds are best regarded as coordinated dithioformic acid ester complexes. Thus an alternate synthesis of these complexes was developed by reacting in-situ generated alkyl dithioformate esters with $\text{Fe}_2(\text{CO})_9$. The formate proton of these ligands can also be removed with LDA resulting in attack of the carbanion at iron. The alkylation of such anionic intermediates allows the isolation of products with an Fe_2SC tetrahedral core and an exocuster sulfonium function. The X-ray diffraction study of one such product has been completed and reveals a thiocarbonyl unit bridging the two iron atoms perpendicular to the iron-iron bond.

O-Ethyl thioesters react with $\text{Fe}_2(\text{CO})_9$ forming products in which the ester is bound to an $\text{Fe}_2(\text{CO})_6$ unit in the same manner as the alkyl dithioformate ligands. However, O-ethyl thioformate reacts with $\text{Fe}_2(\text{CO})_9$ to give a product of the type $[\text{HC}(\text{S})\text{OEt}]\text{Fe}_2(\text{CO})_6$ in which the ethoxy oxygen atom is not coordinated to the metals. An X-ray diffraction study of this material revealed no metal-metal bond and that the two $\text{Fe}(\text{CO})_3$ units are bridged by the thiocarbonyl groups of the esters. The S-alkyl thioesters were discovered to react with $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ to yield diiron hexacarbonyl complexes with both a bridging acyl ligand and bridging thiolate ligand.

Chapter 4. "Reaction Between Triiron Dodecacarbonyl, Alkanethiols and Triethylamine: A New Route to Alkanethiolate Bridged Diiron Hexacarbonyl Complexes"

It has been found that alkanethiolates will react with $\text{Fe}_3(\text{CO})_{12}$ in THF to generate a dinuclear anion, $[(\mu\text{-RS})(\mu\text{-CO})\text{-Fe}_2(\text{CO})_6]^- [\text{M}]^+$ ($\text{M} = \text{Li}, \text{Na}, \text{Et}_3\text{NH}$). This anionic species will react with a variety of electrophiles with loss of a CO ligand to produce $(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6$ complexes ($\text{E} = \text{acyl}, \text{Ph}_2\text{P}, \text{allyl}$ and allenyl). X-ray diffraction studies have been completed for an allyl and allenyl compound. The allyl ligand is bound as a triatomic bridge between the two iron atoms. The allenyl ligand

bridges the metals with two carbons in the fashion of a σ, π -vinyl ligand. The dynamic behavior of the μ -allenyl complexes was studied by means of variable temperature ^1H NMR spectroscopy. Carbon disulfide reacts with $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^- [\text{Et}_3\text{NH}]^+$ and in the presence of alkyl halides $(\mu, \eta^2\text{-RS-C=S})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ type complexes are formed. Methyl isothiocyanate and methyl isocyanate react with the same anionic species with protonation of the addition adduct by the ammonium cation to form products containing μ, η^2 -thiocarbamoyl and μ, η^2 -carbamoyl ligands. Addition of an iron-proton unit across $\text{C}\equiv\text{C}$ bond can also occur to form $(\mu\text{-vinyl})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ compounds. It has also been discovered that the $(\mu, \eta^2\text{-RCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{Me}, \text{Ph}$) complexes will react with two equivalents of LiEt_3H at -78°C to generate RCH_2OLi and $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]^- [\text{Li}]^+$. The reactions of this anion with allyl chloride, propargyl bromide and diphenylchlorophosphine were found to proceed analogous to those of the diiron heptacarbonyl anion.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
<u>Chapter 1.</u> Addition of Alkynyllithium Reagents to (μ -Dithio)bis(tricarbonyliron).	
INTRODUCTION	18
RESULTS AND DISCUSSION	23
EXPERIMENTAL SECTION	54
General Comments	54
Reaction Between (μ -Dithio)bis(tricarbonyliron),	
Cyclopentylmagnesium Bromide and Iodomethane ..	55
Isobutylmagnesium Bromide and Iodomethane	56
Cyclopropylmagnesium Bromide and Iodomethane ..	58
Neopentylmagnesium Chloride and Iodomethane ...	59
para-Tolylmagnesium Bromide and Iodomethane ...	60
Isobutenylmagnesium Bromide and Iodomethane ...	62
Reaction Between (μ -Dithio)bis(tricarbonyliron),	
1-Lithio-1-hexyne and Iodomethane	63
Lithium Phenylacetylde and Iodomethane	65
Lithium Phenylacetylde and Iodoethane	66
Lithium Phenylacetylde and Benzyl Chloride ...	67
Lithium Phenylacetylde and 1-Bromo-2-propanone	68
4-Lithio-2-methyl-1-buten-3-yne and Iodomethane	69
1-Lithio-1-heptyne and Iodomethane	71
1-Lithio-1-heptyne and 1-Bromo-2-propanone	72

Lithium (Trimethylsilyl)acetylide and Iodomethane	73
Lithium (Trimethylsilyl)acetylide and Iodoethane	74
Ethynylmagnesium Bromide and Iodomethane	75
Lithium Phenylacetylide and Acetyl Chloride ...	77
Lithium Phenylacetylide and Pivaloyl Chloride .	78
Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and	
Iodomethane After Warming for 30 min	79
Acetyl Chloride After Warming for 30 min	80
Iodomethane After Warming for 1.5 h	80
Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Trifluoroacetic	
Acid	81
4-lithio-2-methyl-1-buten-3-yne and Trifluoroacetic Acid	82
1-Lithio-1-hexyne and Trifluoroacetic Acid	84
1-Lithio-1-heptyne and Trifluoroacetic Acid ...	85
1-Lithiopropyne and Trifluoroacetic Acid	86
Ethynylmagnesium Bromide and Trifluoroacetic Acid	88
Lithium (Trimethylsilyl)acetylide and Trifluoroacetic Acid	89
Methyl 3-Lithiopropiolate and Trifluoroacetic Acid	91

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylde and	
Trimethylchlorosilane	92
Trimethyltin Bromide	94
Triphenylgermanium Bromide	95
Triphenyltin Chloride	96
Triphenyllead Bromide	97
Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-hexyne	
Trimethylchlorosilane	99
Trimethyltin Chloride	100
Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithiopropyne and Trimethylchlorosilane	101
Reaction Between (μ -Dithio)bis(tricarbonyliron), Methyl 3-Lithiopropiolate and	
Trimethylchlorosilane	102
Trimethyltin Chloride	104
Reaction Between (μ -Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide and Trimethylchlorosilane .	105
Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylde and	
Acetaldehyde	105
Pivalaldehyde	107
Benzaldehyde	109
Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylde and	
Methylmercuric Chloride	111

Methylmercuric Chloride at -78°C	113
Methylmercuric Chloride, 1 h at -78°C and 4.5 h at Room Temperature	114
Methylmercuric Chloride at Room Temperature ...	114
Isomerization of $(\mu\text{-MeHgS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ in the Presence of Lithium Chloride	115
Reaction Between $[\mu\text{-SC}(\text{SnPh}_3)=\text{C}(\text{Ph})\text{S}]\text{Fe}_2(\text{CO})_6$, Phenyllithium and Iodomethane	115
Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Lithium Phenylacetylide and Triphenyltin Chloride in Diethyl Ether	116
Triphenyllead Bromide in Diethyl Ether	117
Addition of $(\mu\text{-Ph}_3\text{PbS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ to a THF Solution of Lithium Bromide	119
Addition of $(\mu\text{-Ph}_3\text{PbS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ and Tri- phenyllead Bromide to a THF Solution of Lithium Bromide	119
Addition of $(\mu\text{-Ph}_3\text{SnS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ to a THF Solution of Lithium Chloride	120
REFERENCES	121
<u>Chapter 2.</u> The Reactivity of $(\text{Di-}\mu\text{-thiol})\text{bis}(\text{tricarbonyl-iron})$ Toward Electrophilic Alkenes and Alkynes.	
INTRODUCTION	128
RESULTS AND DISCUSSION	132
EXPERIMENTAL SECTION	149
General Comments	149
<u>In-Situ</u> Preparation of $(\mu\text{-Dithiol})\text{bis}(\text{tricarbonyl-iron})$	150

Reaction Between (Di- μ -thiol)bis(tricarbonyliron)
and

<u>trans</u> -3-Penten-2-one	150
2-Cyclohexenone	152
Methyl Crotonate	153
Diethyl Maleate	154
Mesityl Oxide	156
Cyclohexylideneacetone	158
5-Methyl-4-Hepten-3-one	160

Attempted Reaction Between (Di- μ -thiol)bis(tricar-
bonyliron) and

3-Methyl-2-cyclohexen-1-one	162
Acetone	163
Methyl 3-Methyl-2-butenolate	163

Reaction Between (Di- μ -thiol)bis(tricarbonyliron)
and

Dimethylacetylene Dicarboxylate	164
Methyl Propiolate	166
3-Butyn-2-one	167
3-Pentyn-2-one	168

REFERENCES	170
------------------	-----

Chapter 3. Diiron Hexacarbonyl Complexes of Thioesters
and Dithioesters.

INTRODUCTION	174
RESULTS AND DISCUSSION	178
EXPERIMENTAL SECTION	228
General Comments	228

Preparation of Methanedithiol	229
Reaction Between Triiron Dodecacarbonyl and Methane-	
dithiol	230
Reaction Between (μ -Methanedithiolato)bis(tricar-	
bonyliron), Lithium Diisopropylamide and	
Iodomethane	231
1-Bromo-2-propanone	232
Iodoethane	233
Benzyl Chloride	234
Allyl Chloride	235
Reaction Between Triiron Dodecacarbonyl and	
α,α -Toluenedithiol	237
Reaction Between (μ -PhHCS ₂)Fe ₂ (CO) ₆ , Lithium Diiso-	
propylamine and	
Iodomethane	238
Iodoethane	239
Reaction Between Cyclopentadienyliron dicarbonyl	
Iodide and Lithium Dithioformate	240
Reaction Between Diiron Nonacarbonyl, Lithium Di-	
thioformate and	
Iodomethane	241
Iodoethane	242
Allyl Chloride	243
Reaction Between (μ -SCHSMe)Fe ₂ (CO) ₆ , Lithium Diiso-	
propylamide and	
Iodomethane	244
Allyl Bromide	245

Reaction Between $(\mu\text{-SCHSEt})\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamine and	
Iodomethane	246
Iodoethane	248
Reaction Between Diiron Nonacarbonyl and	
O-Ethyl Thioacetate	249
O-Ethyl Thiopropanoate	250
O-Ethyl Thioformate	251
Reaction Between $[\mu\text{-SCH(OEt)}]_2\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodomethane	252
Reaction Between Diiron Nonacarbonyl and	
S-Ethyl Thioacetate	253
S-Ethyl Thiobenzoate	255
S-Ethyl Thiopivalate	257
S-Ethyl Thioformate	258
Reaction Between Triiron Dodecacarbonyl and	
S-Ethyl Thioacetate	259
S-Methyl Thioacetate	260
S-Ethyl Thiobenzoate	261
S-Ethyl Thiopivalate	262
An Excess of S-Ethyl Thiobenzoate	262
REFERENCES	263
<u>Chapter 4.</u> Reaction Between Triiron Dodecacarbonyl, Alkanethiols and Triethylamine: A New Route to Alkanethiolate Bridged Diiron Hexacarbonyl Complexes.	
INTRODUCTION	271
RESULTS AND DISCUSSION	274

EXPERIMENTAL SECTION	318
General Comments	318
X-ray Crystallography	319
Reaction Between $\text{Fe}_3(\text{CO})_{12}$, Sodium Ethanethiolate and Acetyl Chloride	324
Reaction Between $\text{Fe}_3(\text{CO})_{12}$, Lithium Ethanethiolate and Acetyl Chloride	324
Reaction Between Triiron Dodecacarbonyl, Ethanethiol and Triethylamine: The Standard <u>In-Situ</u> Generation of $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{Et}_3\text{NH}]$	325
Reaction Between Triiron Dodecacarbonyl, t-Butane- thiol and Triethylamine: The Standard <u>In-Situ</u> Generation of $[(\mu\text{-t-Me}_3\text{CS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{Et}_3\text{NH}]$...	326
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and	
Acetyl Chloride	326
Benzoyl Chloride	327
Diphenylchlorophosphine	327
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and Diphenylchlorophosphine	328
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and	
Allyl Chloride	329
Propargyl Bromide	330
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and	
Propargyl Bromide	331

3-Bromo-3-methyl-1-butyne	332
1-Chloro-2-pentyne	333
Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/$ EtSH/Et ₃ N Mixture and	
1-Bromo-2-propanone	334
1-Bromo-2-propanone at Reflux	334
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture,	
Carbon Disulfide and Benzyl Chloride	335
Carbon Disulfide and Iodomethane	336
Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/$ EtSH/Et ₃ N Mixture and	
Iodomethane	337
Iodomethane at Reflux	338
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and	
Methyl Isothiocyanate	338
Methyl Isocyanate	339
Phenylacetylene	340
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and	
Phenylacetylene at Room Temperature	342
Phenylacetylene at Reflux	342
Acetylene	344
Methyl Propiolate	345
Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and 3-Hexyne	
	346

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$	
Mixture and 3-Hexyne	348
Reaction Between $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, One	
Equivalent of LiEt_3H and Diphenylchlorophosphine ..	351
Reaction Between $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$,	
LiEt_3H and	
Allyl Chloride	352
Propargyl Bromide	353
Reaction Between $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$,	
LiEt_3H and	
Diphenylchlorophosphine	354
Allyl Chloride	355
Reaction Between $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ and LiEt_3H	
Warming to Room Temperature Prior to the Addition	
of Diphenylchlorophosphine	357
REFERENCES	358
BIOGRAPHICAL NOTE	364
ACKNOWLEDGMENTS	365

Chapter 1

Addition of Alkynyllithium

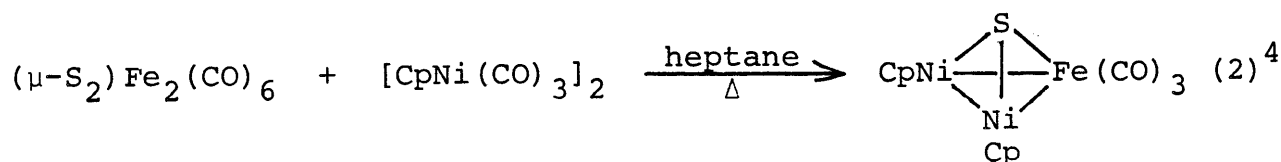
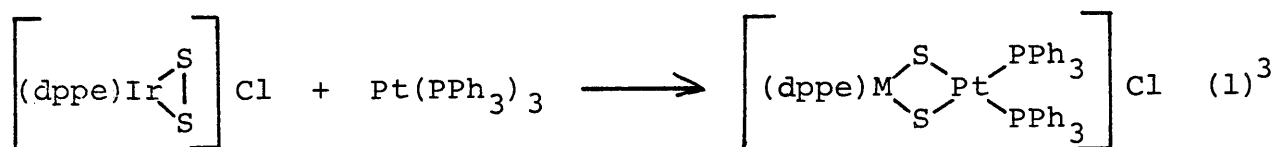
Reagents to

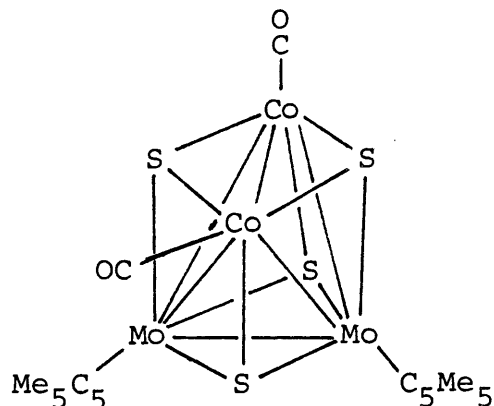
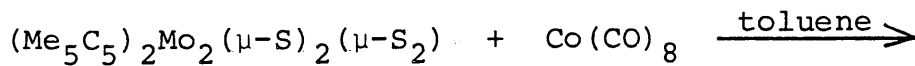
(μ -Dithio)bis(tricarbonyliron)

Introduction

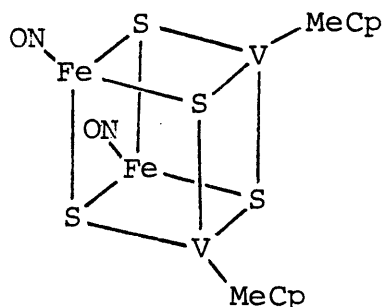
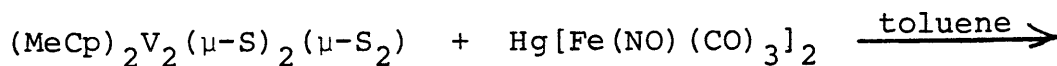
The synthesis and reactivity of transition metal-bound polysulfido ligands have been coming under increased scrutiny. Efforts in this area have produced examples of catenated polysulfide ligands from S_2 to S_5 as chelates or bridged between metal centers. Of this class of ligands, the disulfide group, S_2 , constitutes the largest and most studied of the polysulfide ligands. Recently a review article on the synthesis and properties of disulfide ligands appeared.¹

The majority of the reactivity studies on these compounds has been directed toward the synthesis of sulfido cluster complexes. It has been adequately demonstrated that polysulfido ligands have great potential as reactive moieties. The success of this synthetic strategy has to be attributed to the thiophilicity of the later transition metals and the ability of sulfur to bond to as many as four metal centers at a time.² A few examples of di-, tri- and tetrametallic sulfido complexes formed from disulfido complexes are presented in (eqs.1-5).

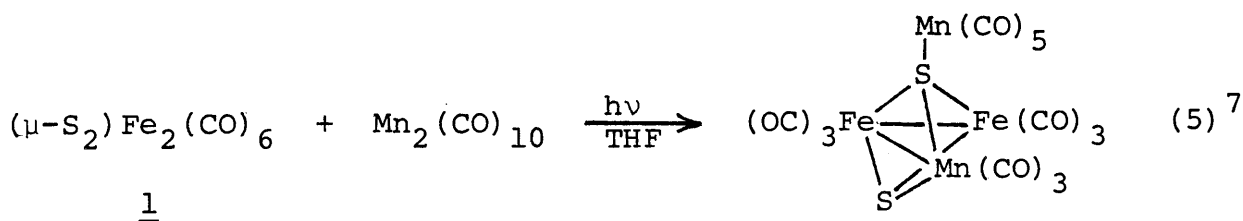




(3)⁵



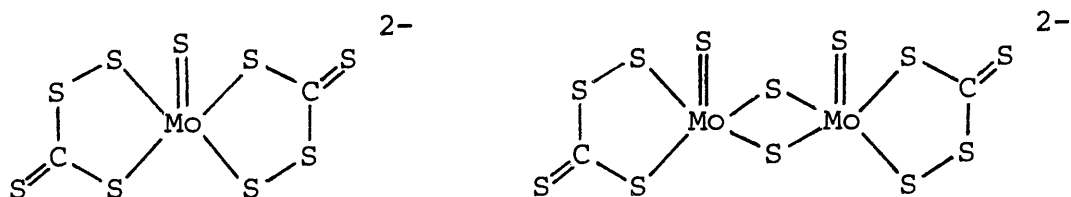
(4)⁶



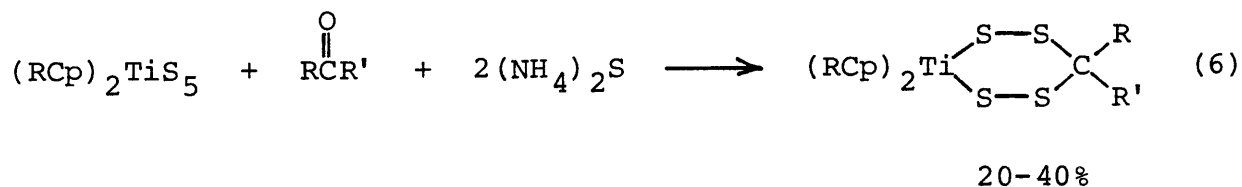
In this regard the documented reactivity of (μ -dithio)bis-(tricarbonyliron), 1, in sulfido cluster synthesis remains unsurpassed.^{4,7,8a-h}

The synthetic potential of polysulfido ligands, however, does not end at cluster synthesis. Examples exist in the

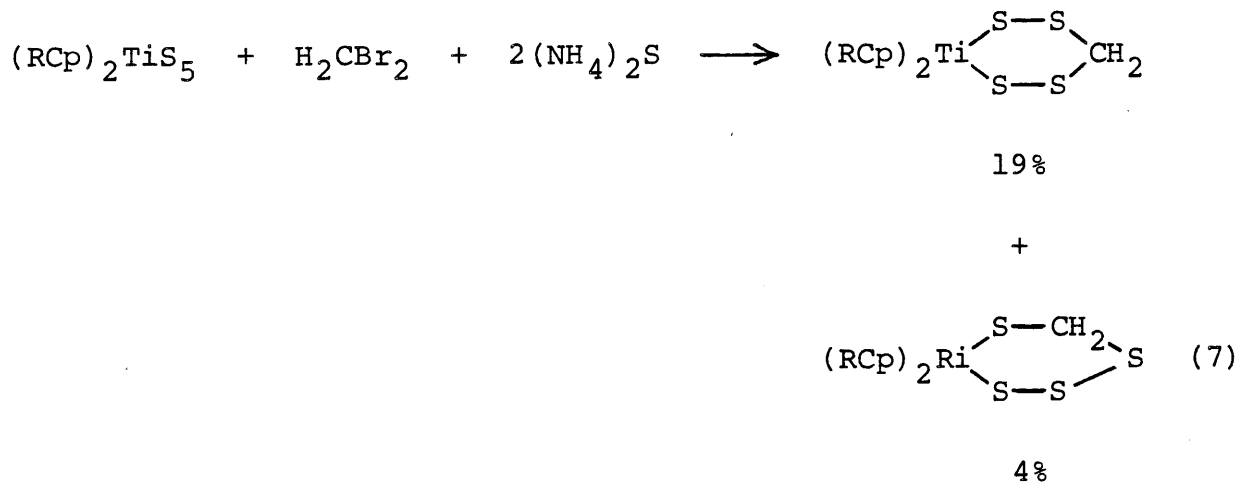
literature of reactive organic molecules interacting with catenated sulfur ligands to produce organic thio ligands. Methylation of the side-on bonded S_2 ligand of $Os(S_2)(CO)_2(PPh_3)_2$ with $CH_3SO_3CF_3$ gave the $[Os(S_2CH_3)(CO)_2(PPh_3)_2]^+$ cation.^{9,10} The analogous reaction occurs with the disulfide ligands of $[Ir(S_2)(dppe)_2]^+$ and $MoO(S_2)(S_2CNMe_2)_2$ when they are treated with CH_3SO_3F .¹¹ Carbon disulfide was found to react with the chelating tetra- and disulfide ligands of $[(S_4)_2MoS]^{2-}$ and $[(S_4)Mo_2S_4(S_2)]^{2-}$ to form perthiocarbonate ligands (CS_4^{2-}) .¹² In a recent report Rauchfuss and Giolando have described the prepara-



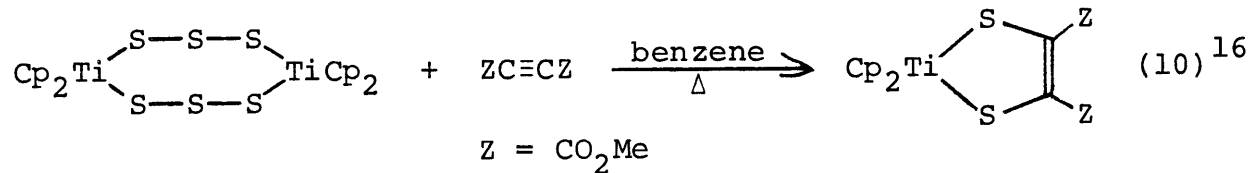
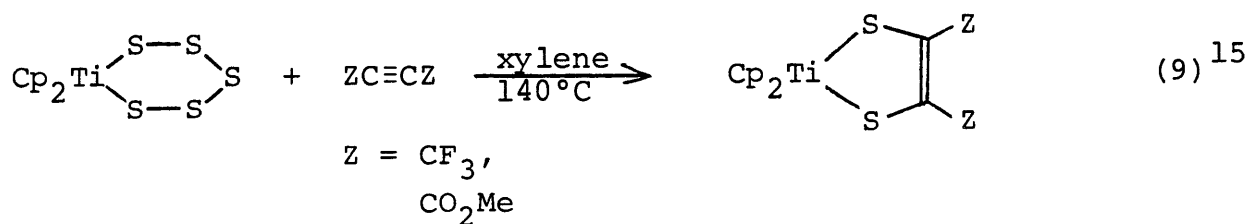
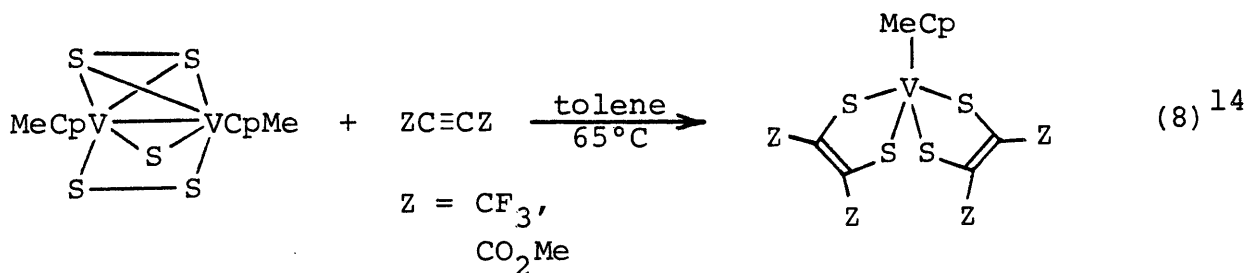
tion of alkylidenebis(perthiolate) ligands from the pentasulfido ligand of $(RCp)TiS_5$ ($R = H, Me, i-Pr$), (eq.6 and 7).¹³

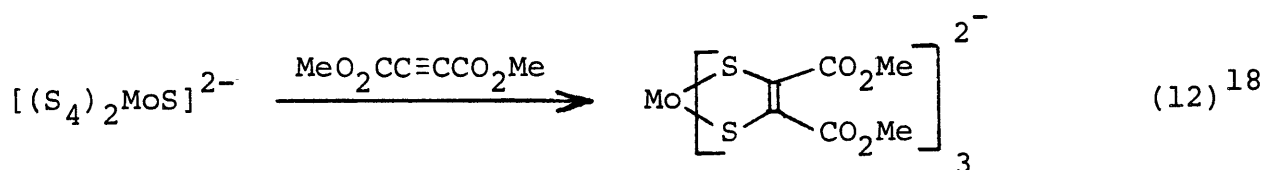
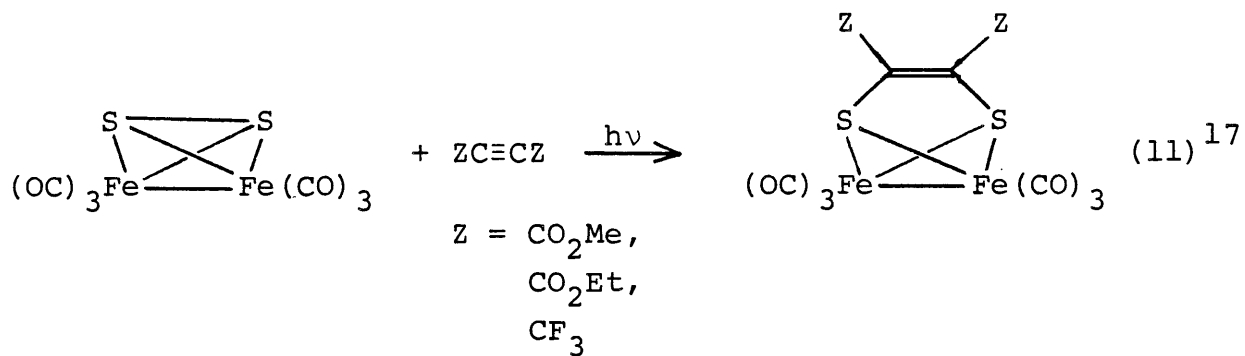


The most common reaction of polysulfido complexes to produce organosulfur ligands is that with electrophilic acetylenes. Generally, this reaction proceeds with insertion of the acetylene into a sulfur-sulfur bond to yield dithiolene



compounds. A partial list of the reported examples of this reaction is given, (eq.8-12). The scope of this reaction for

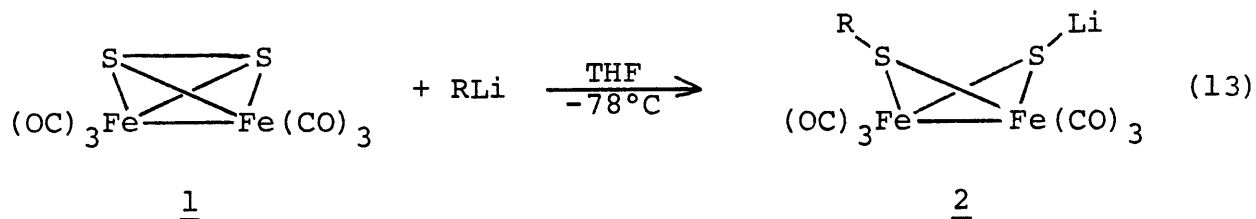




dithiolene ligand synthesis, however, is severely limited in that only the most electrophilic acetylenes react (e.g., hexafluoro-2-butyne, dialkyl acetylene dicarboxylates).¹⁹

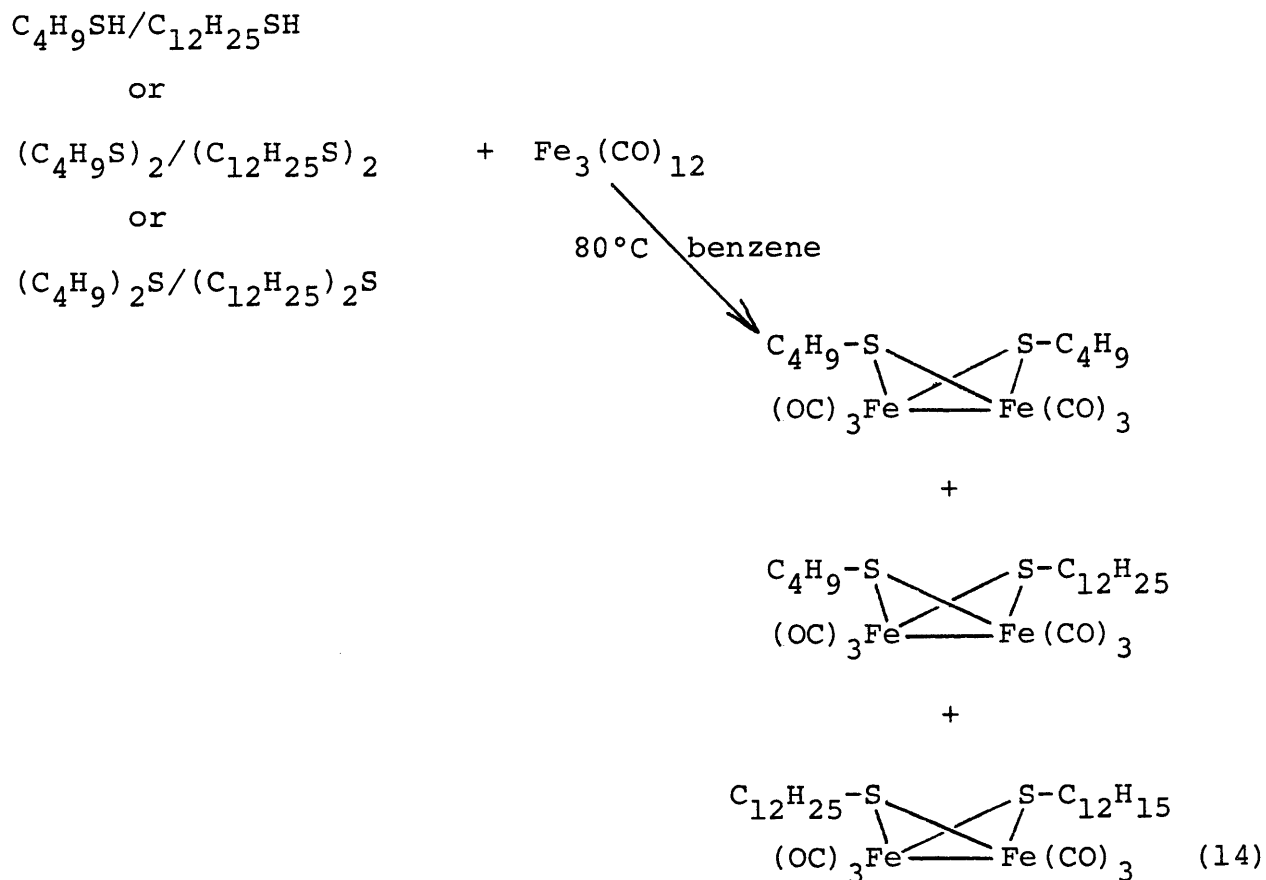
Results and Discussion

The reaction of organic nucleophiles with polysulfido ligands represents an attractive approach to the synthesis of organosulfur ligands based on the precedents of S_8 ^{20,21} and organic disulfide²² reactions with these reagents. Despite this, such studies have only been conducted with μ -dithiobis(tricarbonyliron), 1.²³ Seyferth and Henderson reported that 1 reacted with one equivalent of MeLi or n-BuLi in THF at -78°C, resulting in a red-to-green color change.²⁴ After addition of iodomethane, the isolation of red $(\mu-RS)(\mu-MeS)-Fe_2(CO)_6$ (R = Me, Bu) complexes could be achieved in high yield. The observed green color of the reaction mixture after addition of the lithium reagent was attributed to the formation of a sulfur-centered anionic intermediate, 2 (eq.13). This reaction



provided the first convenient synthesis of diiron hexacarbonyl complexes with two different bridging alkylthiolate groups. Prior to this it had been demonstrated that di- μ -alkylthiolato-bis(tricarbonyliron) complexes were best synthesized from alkylthiols and diiron nonacarbonyl or triiron dodecacarbonyl.^{25,26} Alkyl sulfides and disulfides also can be used, although such reactions generally give lower yields.²⁶ Complexes with two

different alkyl groups can be produced by these methods if mixtures of alkylsulfido compounds are used. However, these reactions proceed to yield all of the possible products (eq.14), which makes them unattractive routes to mixed alkyl complexes of the type $(\mu\text{-R'S})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$.²⁶



X-ray structure determinations have been carried out for $(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ type compounds for $\text{R} = \text{ethyl}$ ²⁷ and phenyl ²⁸ (Fig.1, $\text{R} = \text{Et}$). Compounds of this type exhibit an overall tetrahedral core geometry defined by the iron and sulfur atoms with distorted octahedral coordination spheres around the iron atoms. The crystal structure depicted in Fig.1 demonstrates

that the ethyl groups occupy different positions relative to the core tetrahedron. Using the labelling convention of Shaver, Fig.1 illustrates the e,a isomer (a = axial, e = equatorial).²⁹

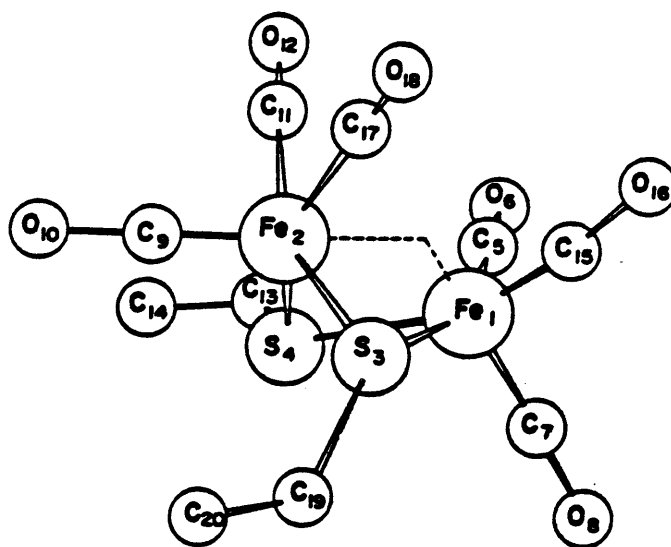
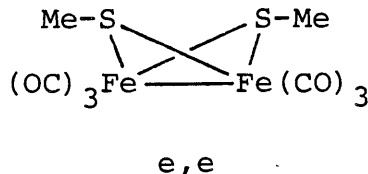
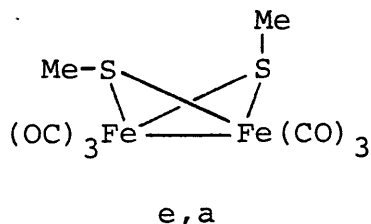


Figure 1. The molecular configuration of $[\text{C}_2\text{H}_5\text{SFe}(\text{CO})_3]_2$.

The equatorial ethyl group (C_{13} and C_{14}) is oriented in toward the iron-iron bond and the axial group (C_{19} and C_{20}) away from the tetrahedral core. R.B. King was the first to demonstrate that isomers of this type were separable by using column chromatography to resolve the e,a and e,e isomers of $(\mu\text{-MeS})_2\text{Fe}_2(\text{CO})_6$, 3. The e,a isomer was eluted from the alumina column first.³⁰ The geometries can be assigned on the basis of the ^1H NMR spectra of the two isomers. The e,e isomer, which has two equivalent methyl groups, shows a singlet at δ 2.07 ppm in its NMR spectrum. The e,a isomer, with two inequivalent methyl



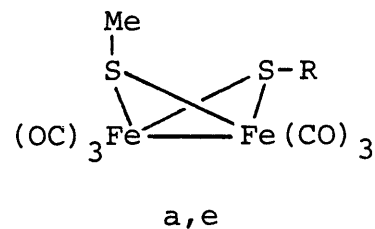
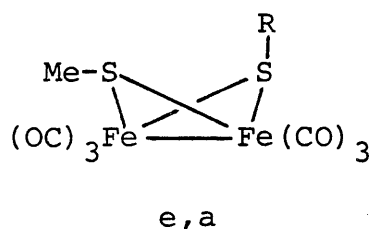
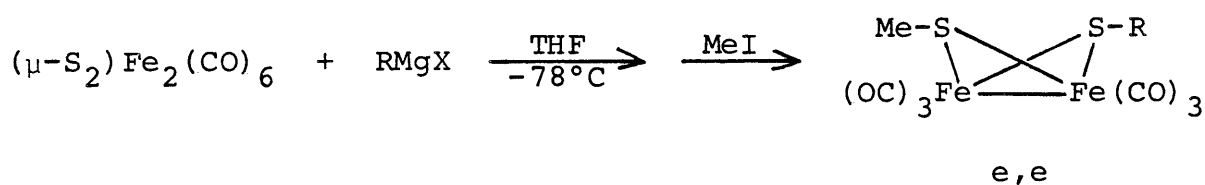
3

groups, has two singlets at δ 2.13 (e) and 1.62 (a) ppm in its NMR spectrum. Note that the resonance of the equatorial methyl groups occur at lower field than those of the axial methyl group. This trend, which subsequently has proven to be general in work conducted in this laboratory, can be used to assign alkyl group orientations in $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ complexes.

In extending the synthetic potential of the reaction represented in eq.13, Song found that Grignard reagents also react with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in THF at -78°C to produce green reaction solutions. Addition of primary alkyl halides to these solutions resulted in the formation of $(\mu\text{-RS})(\mu\text{-R'S})\text{Fe}_2(\text{CO})_6$ compounds. Examples of the variety of Grignard reagents which have been used in this reaction are given in Table 1. As shown in Table 1, these reactions give good yields and generally all three possible geometric isomers are observable by ^1H NMR spectroscopy. The a,a isomer is never formed due to steric constraints.²⁷ Integration of the -SMe signals allowed determination of the isomer ratios.

It was also of interest to determine if alkynyllithium reagents would add to the sulfur-sulfur bond of 1. In previous work it was found that $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ would react with

Table 1

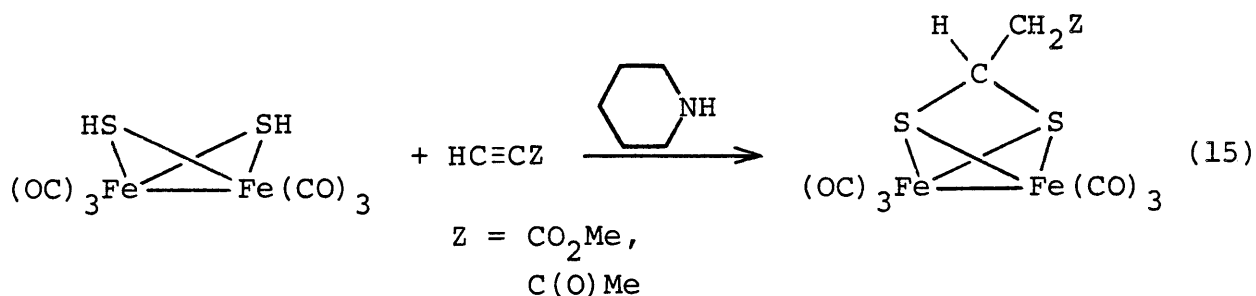


4	R	% Yield	Isomer Ratio <u>e,e/e,a/a,e</u>
a	cyclopentyl ^a	91	
b	isobutyl	99	2.5/1/3.3
c	cyclopropyl	92	1/-/1
d	neopentyl	43	1.3/1/1.3
e	<u>para</u> -tolyl ^b	89	
f	isobutenyl	94	1.6/1/1.9

^aThree isomers were observable by ¹H NMR spectroscopy but their ratio could not be determined due to overlapping SMe and cyclopentyl signals.

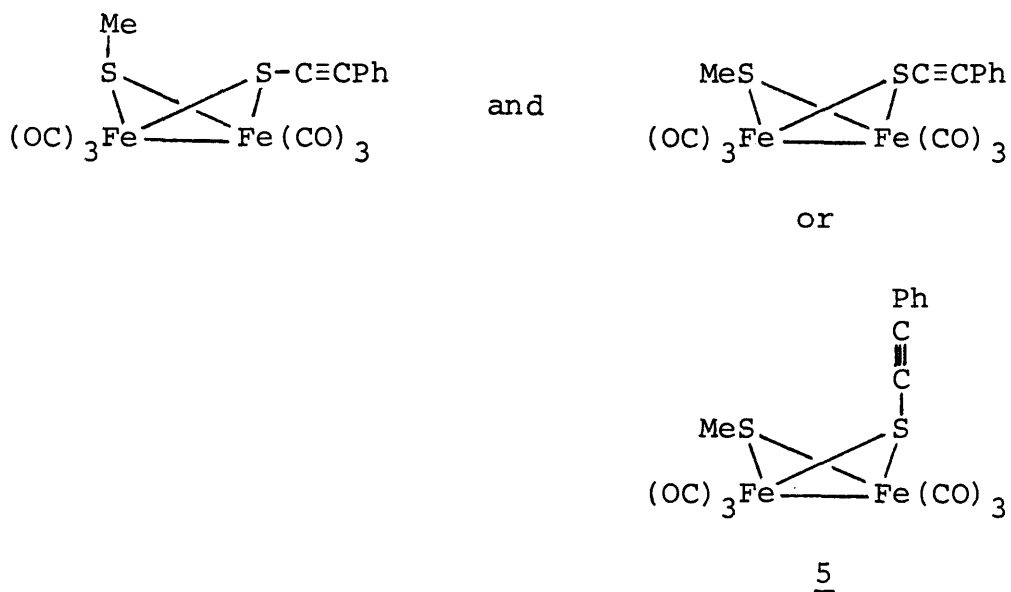
^bTwo isomers were observed in the ¹H NMR spectrum in 4/1 ratio, but isomer geometries could not be determined.

electrophilic acetylenes forming alkylene bridges between the sulfurs, (eq.15).³¹ Since these reactions showed that the base



catalyzed thiol addition of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ to a $\text{C}\equiv\text{C}$ bond was a feasible reaction, the question existed as to whether similar bridging of the sulfur atoms could occur if alkynyllithium reagents were reacted with 1. The expected anionic intermediate of such a reaction would be $(\mu\text{-RC}\equiv\text{CS})(\mu\text{-LiS})\text{Fe}_2(\text{CO})_6$ in which intramolecular thiolate addition to the carbon-carbon triple bond could lead to either one or two carbon bridged products. Thus lithium phenylacetylide was treated with 1 at -78°C in THF, resulting in a green reaction mixture. The solution was quenched at -78°C with an excess of iodomethane (1 h at -78°C and 1 h at room temperature) which caused a green-to-red color change. Isolation of the red crystalline product, mp $80\text{-}100^\circ\text{C}$ dec, gave $(\mu\text{-MeC})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$, 5, in 85% yield as a 1.3/1 (CH_3 a/ CH_3 e) mixture of two isomers. Although the shift values for the SCH_3 ^1H NMR signals were indicative of the axial and equatorial orientations, such geometric information could not be obtained for the $\text{SC}\equiv\text{CPh}$ group. It is quite clear that when the CH_3 groups is axial the alkynyl moiety is

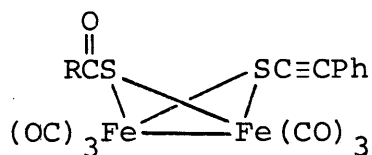
equatorial; however, for the equatorial CH_3 isomer, the orientation of alkynyl group could be in either position. The $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture also was treated with iodoethane, benzyl chloride and 1-bromo-2-propanone all of which produced products analogous to 5. From the iodoethane-



quenched mixture, a red oil was isolated in 75% yield as a 3/1.7/1 (Et a/Et e/Et e) mixture of three isomers. Both benzyl chloride and 1-bromo-2-propanone gave solid products, in 28 and 75% yield, respectively, containing two isomers dominated by the species with the added alkyl group in the axial position; 9/1 (PhCH_2 a/ PhCH_2 e), 13/1 ($\text{MeC}(\text{O})\text{CH}_2$ a/ $\text{MeC}(\text{O})\text{CH}_2$ e). That alkylation occurred at sulfur for these reactions is assured on the basis of the presence of isomers, a medium intensity $\text{C}\equiv\text{C}$ stretching band in the IR spectra in the range 2193 to 2174 cm^{-1} and the presence of signals in the ^{13}C NMR spectra in the range δ_{C} 64.6 to 93.4 assignable to alkynyl carbons.³²

We were surprised that only nonbridging products had formed; but other alkynyllithium reagents also reacted with 1 in THF at -78°C to give $(\mu\text{-R'S})(\mu\text{-RC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ complexes after alkylation. The $\text{Me}_3\text{SiC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ mixture was alkylated with both methyl and ethyl iodide to give crystalline products in 86 and 84% yield, respectively. Both of these compounds exist as mixtures of two isomers, but again, the orientation of the alkynyl group cannot be determined with certainty when the methyl or ethyl group is axial. Other $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixtures, when quenched with iodomethane, $\text{R} = \text{n-butyl}$, n-pentyl and $\text{C}(\text{Me})=\text{CH}_2$, gave sulfur methylated products in 93, 91, and 89%, yield, respectively. For $\text{R} = \text{n-butyl}$ and n-pentyl, isomer ratios could not be determined due to overlap of the SCH_3 and other alkyl signals in the ^1H NMR spectra. However, the ^{13}C NMR spectra did indicate that isomers were present from the number of alkynyl carbon signals; the $\text{R} = \text{n-butyl}$ complex was a mixture of two isomers and the $\text{R} = \text{n-pentyl}$ a mixture of all three. For the isopropenylacetylene-derived complex, $\text{R} = \text{C}(\text{Me})=\text{CH}_2$, two isomers were observed in the ^1H NMR spectrum in a ratio of 5/1 ($\text{CH}_3 \text{ e}/\text{CH}_3 \text{ a}$). Even ethynylmagnesium bromide reacted with 1 at -78°C , producing a green solution, methylation of which yielded $(\mu\text{-MeS})(\mu\text{-HC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ as a 3/1 ($\text{CH}_3 \text{ a}/\text{CH}_3 \text{ e}$) mixture of isomers, mp $95\text{-}100^{\circ}\text{C}$ dec, in 77% yield.

Addition of acid chlorides to the green $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ intermediate at -78°C led to the novel bridging thioester complexes, 6a and 6b, in 92 and 67% yield, respectively. Both 6a and 6b were isolated as solids with only one isomer



6a, R = Me

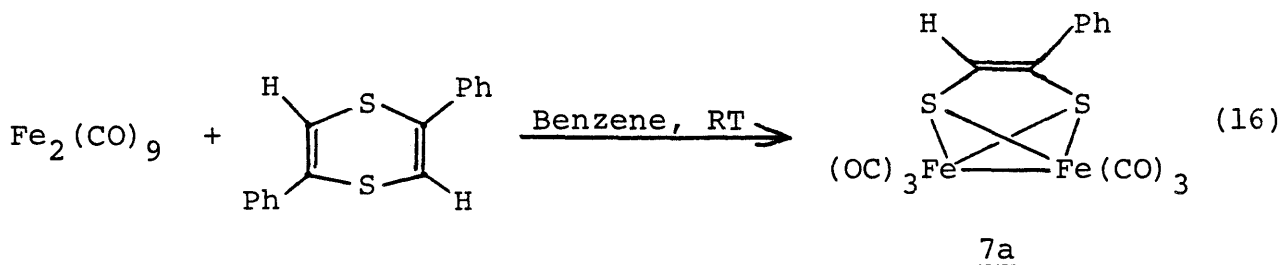
b, R = t-Butyl

present. The orientation of the acyl groups as either axial or equatorial could not be determined.

Since only sulfur-alkylated or -acylated products were isolated from the $\text{RC} \equiv \text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture when quenched at -78°C , it was wondered whether addition of the alkyl halide at room temperature could yield a cyclized product. This proved not to be the case. When the $\text{PhC} \equiv \text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ was removed from the dry ice/acetone cold bath and stirred for 30 min prior to addition of iodomethane, only 5 was isolated in 84% yield. Using the same procedure, acetyl chloride also yielded only the sulfur-acylated product, 6a, isolated in 61% yield. Thus, warming of the $\text{RC} \equiv \text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ mixture led to no difference in the course of the reaction. However, when such a mixture was stirred for 1.5 h after removal from the cold bath, a substantially lower yield, 33%, of 5 was isolated after addition of iodomethane, indicating that the $\text{RC} \equiv \text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ anionic intermediate is of limited stability at room temperature.

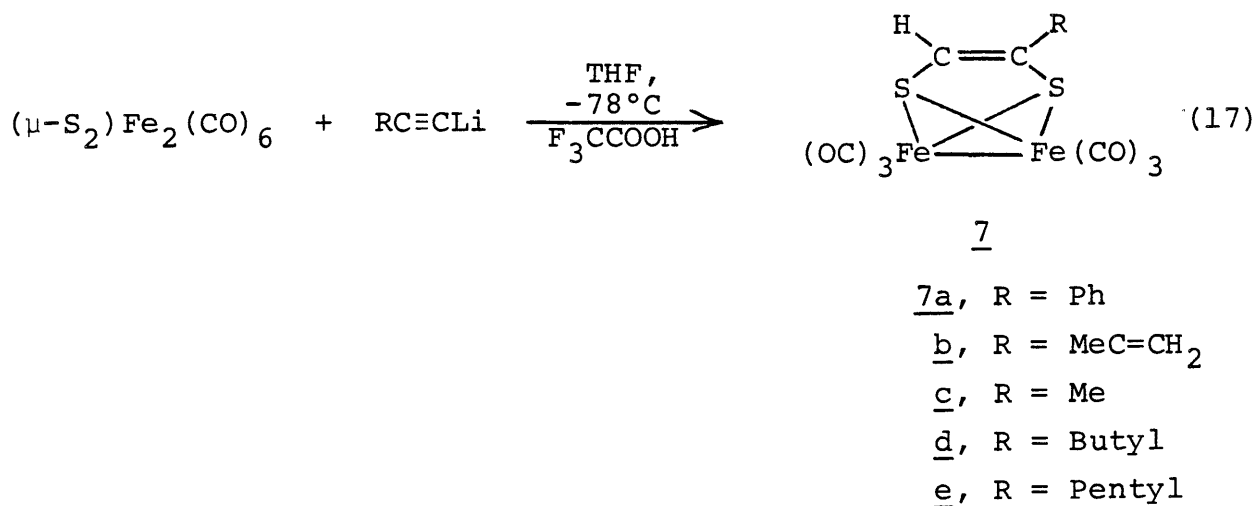
Protonation of the $\text{PhC} \equiv \text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture at -78°C with $\text{CF}_3\text{CO}_2\text{H}$, however, did not result in the isolation of $(\mu\text{-HS})(\mu\text{-PhC} \equiv \text{CS})\text{Fe}_2(\text{CO})_6$. Instead, a dithiolene complex,

7a, was isolated in 87% yield. The structure of 7a was ascertained from spectral data. The ^1H NMR spectrum revealed a vinyl proton resonances at δ 6.46 ppm, and the ^{13}C NMR spectrum showed no signals due to alkynyl carbons but did show two vinyl resonance at δ_{C} 134.4 (d, $J = 183\text{Hz}$) and 161.7(s) ppm.³³ Unambiguous proof of the structural assignment was achieved by direct comparison of our product to an authentic sample of 7a synthesized by the method of Bird and Hollins, (eq.16).³⁴



Samples of compound 7a synthesized by protonation of the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture or by the method of eq.14 proved identical on the basis of their ^1H NMR and IR spectra and mixed melting point.

Although alkylation of the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ mixtures failed to produce bridging complexes, the formation of $\text{Fe}_2(\text{CO})_6$ -complexes with dithiolene ligands from the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{-Fe}_2(\text{CO})_6$ system upon protonation has been found to be general for $\text{R} = \text{alkyl, phenyl and C(Me)=CH}_2$, (eq.17). Ethynylmagnesium bromide, $\text{HC}\equiv\text{CMgBr}$, also reacted with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ to yield, after protonation, a dithiolene compound in 53% yield, mp 55-56°C (lit.³⁵, mp 54-55°C). It was confirmed to be a 1,2-dithiolene complex since only a single vinyl carbon resonance in



the ¹³C NMR spectrum at δ_C 146.3 ppm (d, J = 190Hz) was observed. This ruled out the isomeric 1,1-dithiolene complex for which two vinyl carbon signals would be expected. When R in RC≡CLi is alkyl (eg. methyl, n-butyl, n-pentyl), products of type 7 were obtained in 76, 92 and 77% yield, respectively. The structural assignment of these three compounds could be made on the basis of the absence of vicinal coupling between the vinyl and allylic protons which would be expected for a 1,1-dithiolene structure (allylic coupling, J = 1.7Hz, was observed for R = Me).

Protonation of the Me₃SiC≡CLi/(μ-S₂)Fe₂(CO)₆ reaction mixture, however, led to the isolation of two products, 8a (29%) and 8b (45%), which could be separated by column chromatography (silicic acid/pentane). The mass spectra and combustion analysis of these two compounds indicated they were isomers. In addition, the ¹H and ¹³C NMR spectra revealed they both had vinyl functions, indicating dithiolene structures

for both. Comparison of their vinyl carbon shifts with those of the other complexes already prepared allowed assignments of their structures to be made. Thus the ^{13}C NMR spectrum of 8b, which was eluted from the column after 8a, revealed two similar vinyl carbon shifts at δ_{C} 150.8 (d, $J = 184\text{Hz}$) and 159.7(s), within the range of values reported for the 1,2-dithiolene compounds 7, Table 2. This information supports the assignment of 8b as having the 1,2-dithiolene structure. The other isomer, 8a, obviously had the 1,1-dithiolene structure. Its vinyl carbon shifts, δ_{C} 115.4 (d, $J = 142\text{Hz}$) and 157.9(s), are in agreement with this conclusion since they are not as similar to each other as those in 8b which can be attributed to the one carbon bridge structure. There is also a significant upfield shift of carbon A, δ_{C} in 115.4, in 8a (Table 2) which lies considerably outside the range of carbon A shifts reported for the 1,2-dithiolene ligands.

Two rather different vinyl carbon chemical shifts were observed for product, 9, obtained from the protonation of the $\text{LiC}\equiv\text{CCO}_2\text{Me}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture. For this reason, 9, isolated in 51% yield, was assigned the 1,1-dithiolene

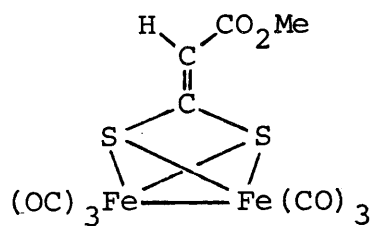
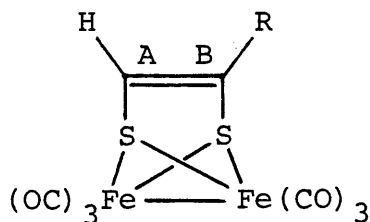
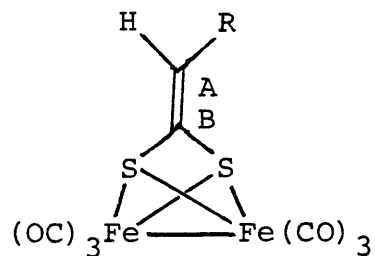


Table 2. ^{13}C NMR Spectra of



Type I



Type II

R	Type	δ	
		Carbon A	Carbon B
H ^b	I	146.3 (d, J = 190Hz)	--
CH ₃	I	134.2 (d, J = 183Hz)	159.5
n-C ₄ H ₉	I	133.4 (d, J = 183Hz)	164.4
n-C ₅ H ₁₁	I	133.4 (d, J = 183Hz)	164.4
C ₆ H ₅	I	134.4 (d, J = 183Hz)	161.7
CH ₃	I	135.7 (d, J = 183Hz)	162.8
C=CH ₂ ^c			
(CH ₃) ₃ Si	I	150.8 (d, J = 184Hz)	159.7
(CH ₃) ₃ Si	II	115.4 (d, J = 142Hz)	157.9
CO ₂ CH ₃ ^c	II	108.4 (d, J = 169Hz)	165.3

^aSolvent used was CDCl₃ unless stated otherwise.

^bSolvent was CD₃CN.

^cSolvent was CD₂Cl₂.

structure. Table 2 reports the high field vinyl carbon resonance for 9 at δ_C 108.4 (d, J = 169Hz) which is uncharacteristic of the 1,2-dithiolene compounds.

Previous to these studies dithiolene complexes of diiron hexacarbonyl were confined to a few symmetrical systems.³⁶ Henderson found that electrophilic acetylenes insert into the sulfur-sulfur bond of 1 upon UV irradiation.¹⁷ Earlier, Schrauzer had reported that such complexes could be formed by a ligand transfer reaction from $M(S_2C_2R_2)_2$ (M = Fe, Co, Ni) to $Fe(CO)_5$.^{35,37} An X-ray crystal structure determination of $(\mu-Ph_2C_2S_2)Fe_2(CO)_6$, 10, confirmed this structure, Fig.3.³⁸ A 1,1-dithiolene complex of diiron hexacarbonyl has recently been reported by Lewis and co-workers.³⁹ This compound, 11, the structure of which is depicted in Fig.4, was isolated in 1-2% yield as one of five reported products from the reaction of $Fe_3(CO)_{12}$ and CS_2 .

Since protonation of the $RC\equiv CLi/(\mu-S_2)Fe_2(CO)_6$ reaction mixtures proved to be a general and useful method for the synthesis of diiron hexacarbonyl dithiolene complexes, while alkylation and acylation had given "unbridged" products, reactions of such $RC\equiv CLi/(\mu-S_2)Fe_2(CO)_6$ reaction mixtures with other electrophiles were of great interest since it was not clear as yet whether "bridged" or "open" products would be formed. With this question in mind, some Group IVA metal halides were investigated as the electrophilic reagents. Equation 18 illustrates the synthesis of 8b in 40% yield by the addition of Me_3SiCl to the $HC\equiv CMgBr/(\mu-S_2)Fe_2(CO)_6$ reaction solution at

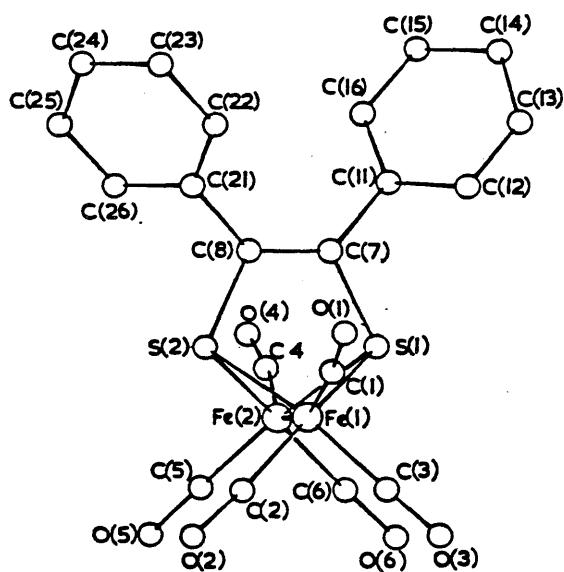


Figure 3. The molecular structure of 10.

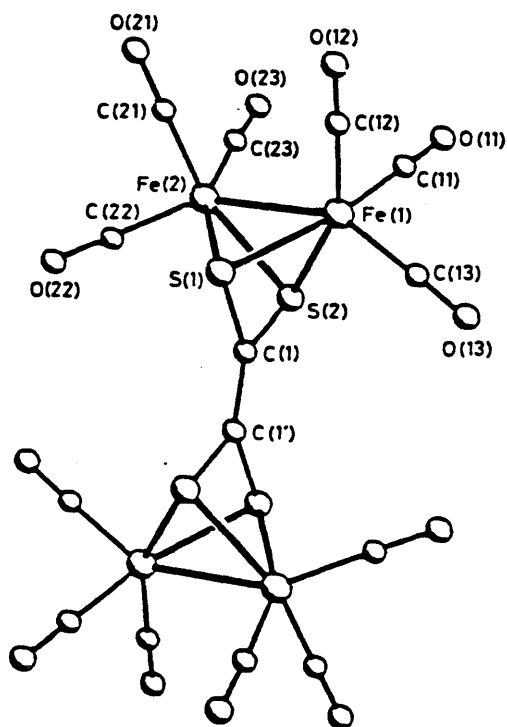
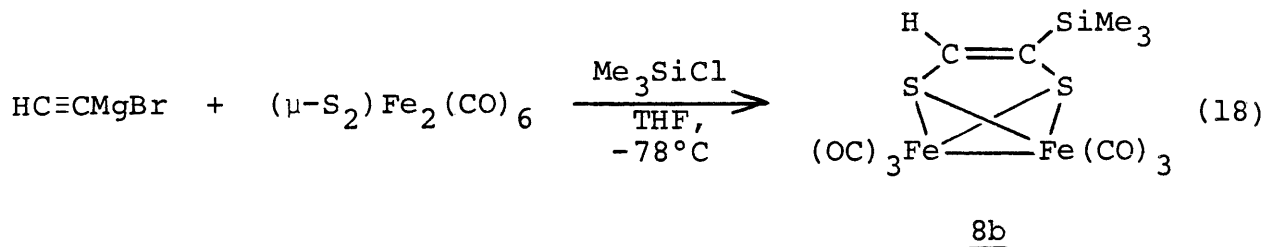
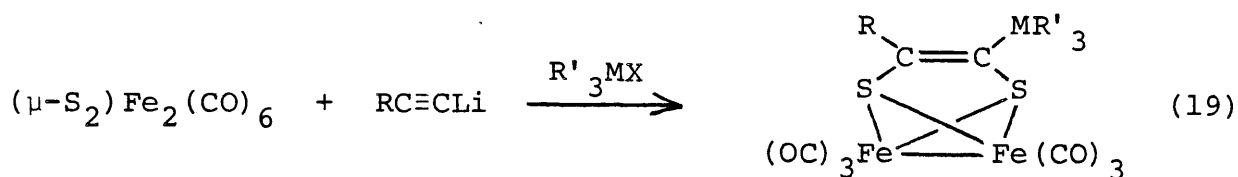


Figure 4. The molecular structure of 11.



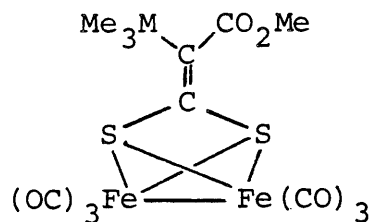
-78°C. This reaction yielded only 8b giving none of the 1,1-dithiolene isomer, 8a, which had been isolated from the protonation of the $\text{Me}_3\text{SiC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture and none of the "open" isomer. This result suggested that the Group IVA metal halides would also yield dithiolene complexes and that the structure of these products would correspond to those obtained in the trifluoroacetic acid-quenched reactions (eg. 1,1- or 1,2-dithiolene complexes). This was borne out by extending the quenches to include Ph_3GeBr , Me_3SnCl , Me_3SnBr , Ph_3SnCl , and Ph_3PbBr , (eq.19). In general, a two- or three-fold excess of the trialkyl- or triarylmatal halide was added to the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture at -78°C, and, after stirring for 30 min, the mixture was allowed to warm to room temperature. Purification of the products was easily accomplished by column chromatography (silicic acid) and recrystallization. Table 3 reports the vinyl carbon shifts observed in the ^{13}C NMR spectra of the Me_3Si and Me_3Sn derivatives synthesized in this manner. For these compounds assigned structure Type I the vinyl carbon shifts are found in the range of δ_{C} 143.7 to 170.3. The high field signals have been assigned to the metal-substituted vinyl carbons since this is the trend reported for various vinyl silanes and stannanes. Two compounds



R	M	R'	% yield
H	Si	Me	40
Me	Sn	Me	75
Ph	Si	Me	66
Ph	Sn	Me	91
Ph	Sn	Ph	86
Ph	Ge	Ph	41
Ph	Pb	Ph	70
<u>n</u> -butyl	Si	Me	82
<u>n</u> -butyl	Sn	Me	86

which illustrate this trend are trans-Me₃SiCH=CHPh⁴⁰ and cis-Me₃SnCH=CHMe₃⁴¹ for which the metal substituted vinyl carbon signals occur at δ_C 129.3 and 129.7, respectively; at lower field the signals at δ_C 143.7 and 143.4, respectively, were assigned to the vinyl carbon β to the metal.⁴²

As previously observed in Table 2, a structure change in the products obtained from the F₃CCO₂H quenched reactions could be determined from the ¹³C NMR spectra. A shift of one of the vinyl carbons to higher field indicated the formation of a 1,1-dithiolene ligand. When Me₃SiCl or Me₃SnCl was added to the LiC \equiv CCO₂Me/(μ -S₂)Fe₂(CO)₆ reaction mixture, red crystalline products, 12a and 12b, were observed in 69 and 40% yield, respectively. Both had a vinyl carbon resonance at higher field, outside the range of those shifts reported for the two



12a, M = Si

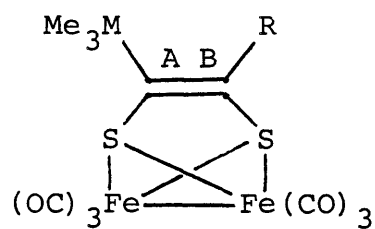
b, M = Sn

carbon-bridged complexes, Table 3. Since no other spectroscopic data could indicate this subtle structural difference, the assignment of the Group IVA metal derivatives as either one or two carbon-bridged had to be made solely on the basis of their ^{13}C NMR spectra.

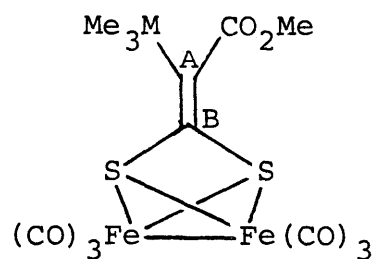
A rational mechanism explaining the experimental results thus far reported has to account for the formation of both open (sulfur-quenched) and cyclized (carbon-quenched) products. These observations could be explained in terms of an equilibrium between an open S-centered anion and closed C-centered anion, Scheme 1. This would provide an explanation for the formation of 1,1-dithiolene ligands, since 15 is a reasonable intermediate when R is capable of stabilizing an α -carbanion. This indeed corresponds to the experimental results since one carbon-bridged complexes have only been formed when $\text{R} = \text{SiMe}_3$ or CO_2Me . Both the Me_3Si ⁴³ and CO_2Me ⁴⁴ groups are known to stabilize α -carbanions.

Although phenyl and vinyl groups provide resonance stabilization to α -carbanions, one carbon-bridged products were not obtained when R was a phenyl or $\text{H}_2\text{C}=\text{CMe}$ group. The resonance

Table 3. ^{13}C NMR Data for



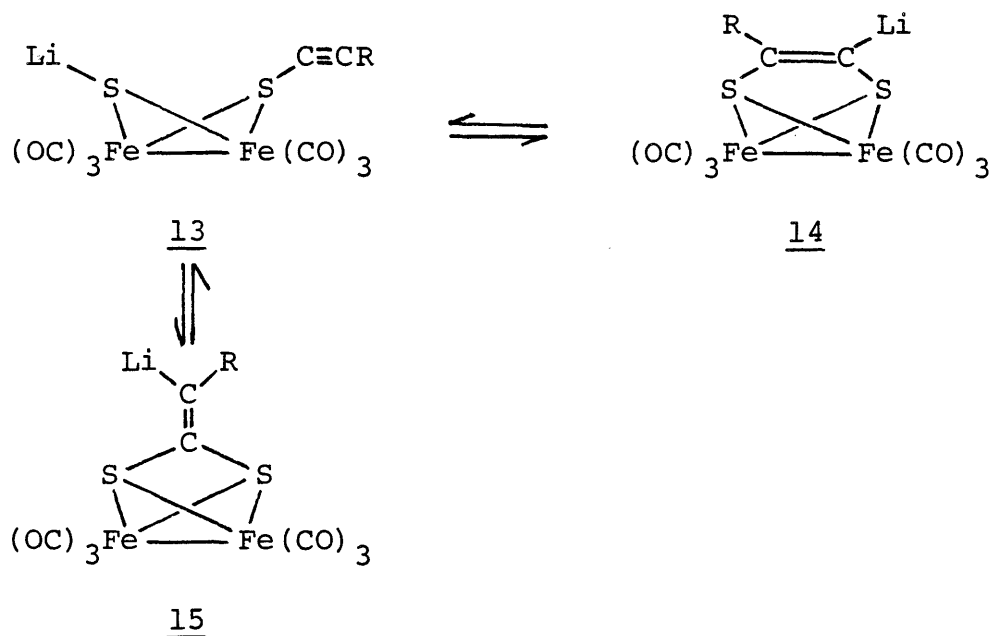
Type I



Type II

<u>R =</u>	<u>M</u>	<u>Type</u>	<u>δ Carbon A</u>	<u>δ Carbon B</u>
H	Si	I	159.7	150.8
$n\text{-C}_4\text{H}_9$	Si	I	143.7	170.3
C_6H_5	Si	I	148.6	167.2
CH_3	Sn	I	143.7	163.8
$n\text{-C}_4\text{H}_9$	Sn	I	143.8	169.2
C_6H_5	Sn	I	149.5	167.7
CO_2Me	Si	II	121.8	165.4
CO_2Me	Sn	II	121.7	165.5

^aSolvent used was CDCl_3 .



Scheme 1

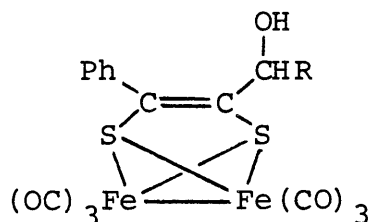
stabilization provided by these two groups is apparently not great enough to allow formation of type 15 intermediates. In these cases the greater stability of the two carbon-bridged intermediate, 14, is attributed to the α -sulfur atom, also capable of stabilizing an adjacent carbanion,⁴⁵ and to less ring strain associated with the diatomic bridge. The small S-C-S bond angle of 101.2° reported for 11,³⁹ as opposed to the bond angles of the vinyl carbons in 10,³⁸ approximately 115° for the S-C=C angle, demonstrate the greater ring strain of the 1,1-dithiolene structure.

Low temperature ¹³C NMR studies (THF-d₈, 67.9MHz) of two RC≡CLi/(μ -S₂)Fe₂(CO)₆ reaction mixtures (R = n-C₅H₁₁, SiMe₃) failed to provide evidence for the existence of vinyl carbanion intermediates. The spectrum of the n-C₅H₁₁C≡CLi/(μ -S₂)Fe₂(CO)₆

mixture contained two peaks at δ_C 82.0 and 80.8 at -68°C which remained invariant at the other temperatures (-38 , -13 and 12°C) studied. These two peaks are shifted, one to higher and one to lower field, from those of the alkyne carbons of the neutral compounds $(\mu\text{-n-C}_5\text{H}_{11}\text{C}\equiv\text{CS})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{Me}$, $\text{CH}_2\text{-C(O)Me}$) in which the two types of alkyne carbons appear at approximately δ_C 70 and 90. The same trend was found in the ^{13}C NMR spectra of the $\text{Me}_3\text{SiC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ system, in which two peaks appeared at δ_C 109.5 and 83.3 at -63 , -43 , and 0°C . A peak at 0.16 was assigned to the trimethylsilyl carbons. The observance of just two peaks in the alkene/alkyne carbon shift region of these spectra indicate that either just one intermediate was detected or the time averaged spectra of the interconverting intermediates (Scheme 1) were obtained. Since these signals appear in the region found for the alkyne carbon shifts of the $(\mu\text{-RC}\equiv\text{CS})(\mu\text{-R'S})\text{Fe}_2(\text{CO})_6$ complexes (δ_C 99.3 to 64.6), the dominant anionic intermediate in the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ system would appear best described as 13, the sulfur anion species.

Extending the types of electrophiles which were added to the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction system provided more information concerning the proposed mechanism (Scheme 1). Thus using aldehydes as the electrophile yielded the dithiolene complexes 16 after acidic work up. These are the only compounds formed from the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ mixture to have organic groups on both dithiolene carbons. The chemical shifts of the two vinyl carbons in the ^{13}C NMR spectra of compounds

of type 16 are quite similar, the largest difference occurring for 16a where the shifts are δ_C 151.6 and 155.8. Thus the



16a, R = Me

b, R = Ph

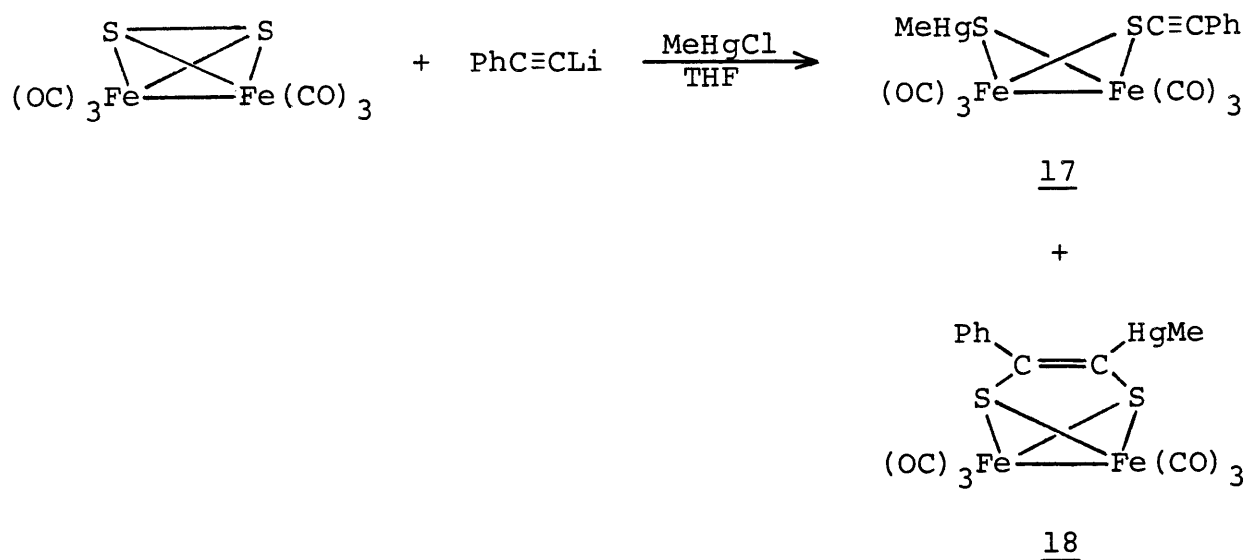
c, R = t-Butyl

aldehydes intercepted vinyl carbanion intermediates in the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ system. If thiolate addition to an aldehyde, the other possible reaction, did occur, it would be expected to be a reversible reaction,⁴⁶ thus not preventing the aldehyde from eventually reacting with a carbanion. Reversible addition to the sulfur anion intermediate, 13, would thus provide a convenient explanation for the formation of cyclized products and the absence of sulfur quenched products in some cases. Unfortunately, other carbonyl compounds, acetone, benzophenone and methyl acetate failed to react with the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture, using the same conditions under which the aldehydes reacted.

The use of MeHgCl as the quench for the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture allowed further investigation into the formation of cyclized versus open products. When MeHgCl was added to the reaction mixture at -78°C , an immediate reaction was observed, signaled by a color change of green-to-red.

Analysis of the mixture by TLC (Baker, silica gel; eluting with pentane) indicated the formation of a single red product. After stirring for 30 min at -78°C the solution was removed from the dry ice/acetone bath and allowed to warm, whereupon a second product began to form as indicated by TLC. Thirty minutes after removal from the cold bath, the solvent was removed and the residue chromatographed. The two isomers 17 and 18 were isolated, Table 3. The TLC monitoring indicated 17 to be the product formed at -78°C . This was borne out by a second experiment in which the reaction solution was stirred at -78°C for 4.5 h; TLC analysis showed only one product. The solvent was immediately removed on a rotary evaporator upon removal of the solution from the cold bath, which thus minimized the formation of 18. This allowed the isolation of 17 in 79% yield and reduced the yield of 18 to 6%. However, simply stirring this reaction mixture at room temperature for 4.5 h, after addition of MeHgCl at -78°C and stirring for 1 h, resulted in the isolation of 18 in 53% yield and none of 17. It was apparent from these experiments that 17 was being formed at -78°C and was isomerizing to 18 as the reaction mixtures were allowed to warm. This was confirmed in separate control reactions. Recrystallized 17 was stable in THF; after stirring for 19 h at room temperature, it could be quantitatively re-isolated. However, in the presence of a stoichiometric quantity of LiCl , 17, dissolved in THF, was converted within 3 h to 18 in 78% yield, (eq.21). These reactions definitely proved that 17 was being converted to 18 but that LiCl was necessary

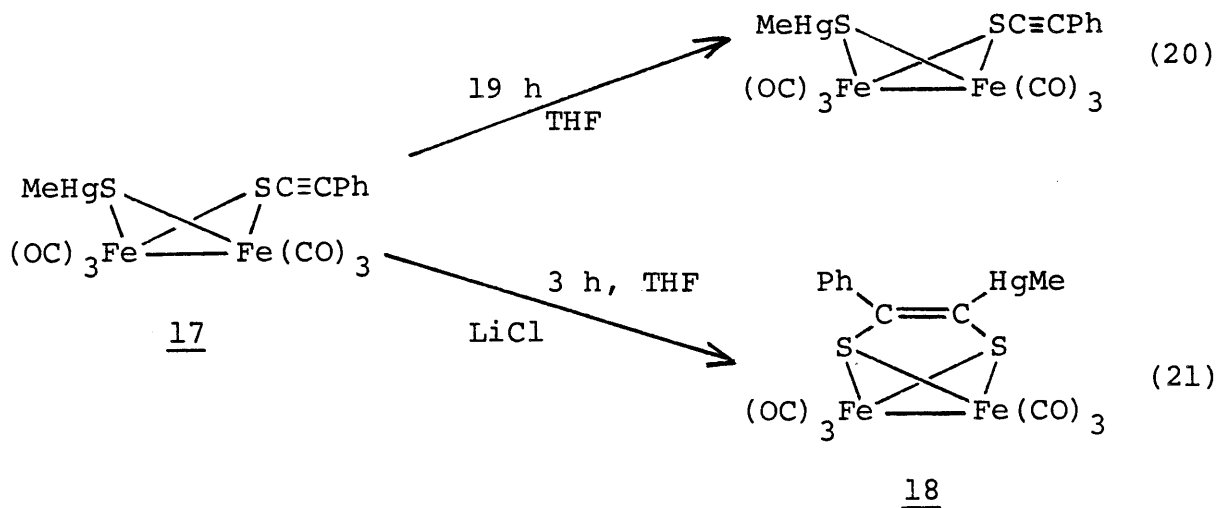
Table 4



<u>Reaction Time (h)</u>		<u>% Yield</u>	
<u>-78°C</u>	<u>RT^a</u>	<u>18</u>	<u>19</u>
.5	.5	52	16
4.5	-	79	6
1	4.5	--	53
-	5 ^b	--	67

^aTime stirred after removal from cold bath.

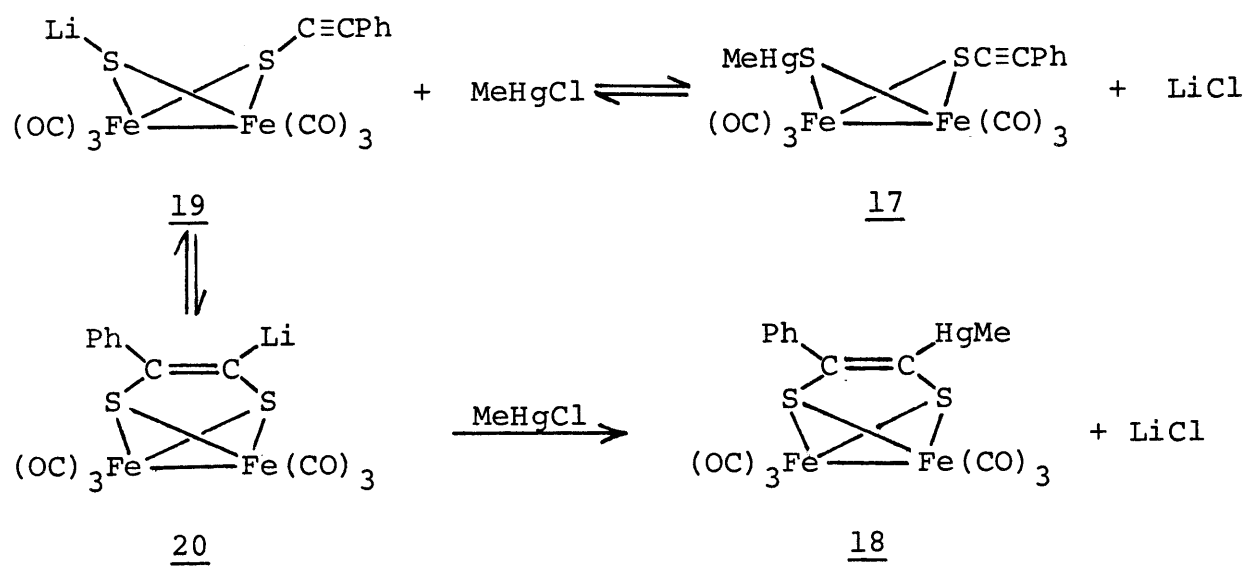
^bThe PhC≡CLi/(μ-S₂)Fe₂(CO)₆ solution was stirred for 35 min after removal from the cold bath prior to addition of MeHgCl.



to promote the ring closure.

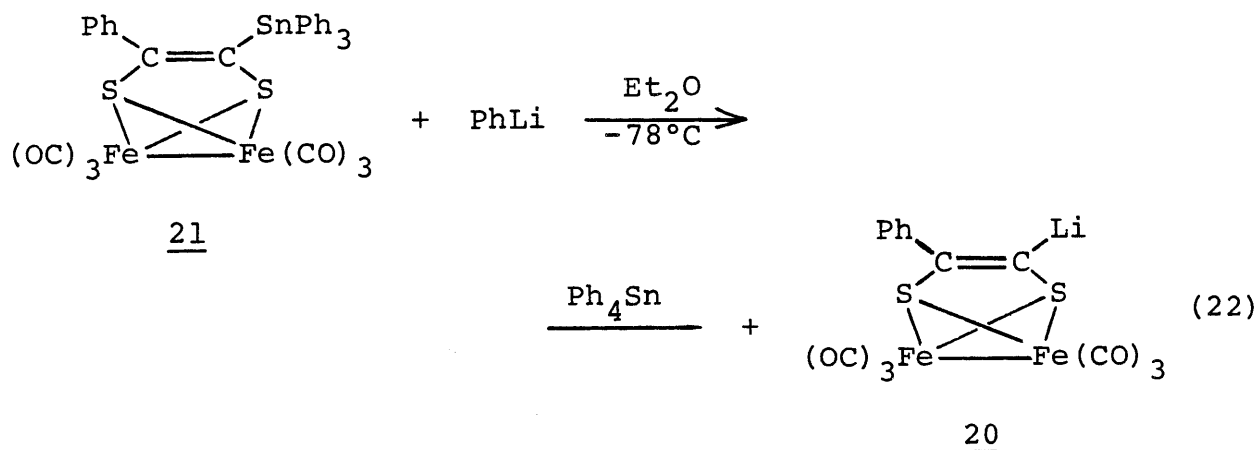
Mechanistically these reactions can still be explained in terms of Scheme 1 (i.e., equilibrium between sulfur and vinyl anion intermediates) if addition of MeHgCl to the sulfur anion is reversible. From the above experiments it is obvious that 17 is formed first at -78°C and upon warming is converted to 18, a process which necessitates the cleavage of an Hg-S bond and the formation of an Hg-C bond. Since LiCl is necessary to promote the isomerization, its function may be to provide a pathway for Hg-S bond scission. A reasonable means by which this could occur would be nucleophilic attack of chloride ion at mercury in 17, reforming MeHgCl and the thiolate species 19, Scheme 2. Once 19 is regenerated, it has, in effect, more opportunity to cyclize to the vinyl anion intermediate, 20, giving MeHgCl another nucleophile with which to react, thus allowing the formation of 18. As 18 is formed irreversibly under the reaction conditions, the reaction stops at this point as the MeHgCl is consumed by 20. Thus the key steps

Scheme 2



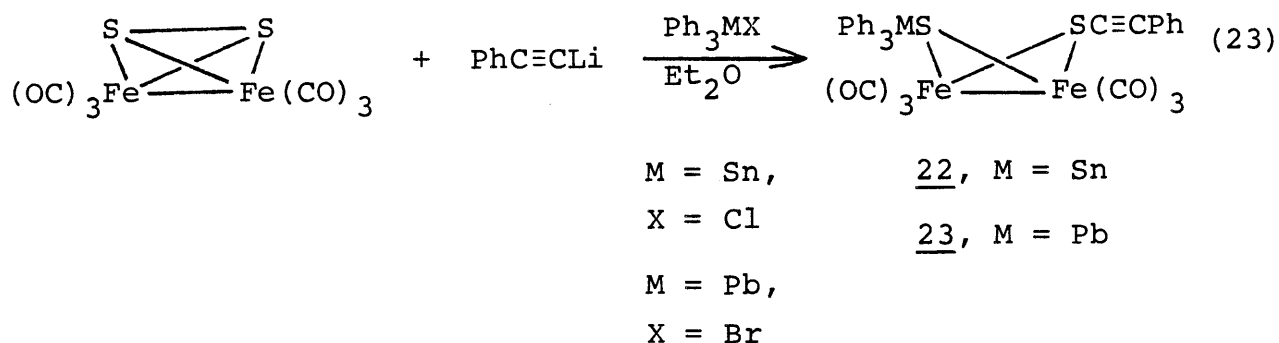
which allow the formation of 18 from the $\text{PhC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2^-(\text{CO})_6$ reaction mixture would be reversible thiolate addition to MeHgCl and an equilibrium between 19 and 20.

It has already been shown that an open type product, 17, can be converted to a cyclized product, 18, which is presumed to involve anionic intermediates. If the equilibrium presented in Scheme 1 indeed occurs, then it should be possible to convert a cyclized product to an open type product if the cyclized compound can be reconverted to its anionic precursor, the vinyl anion. Such a reaction proved possible by use of the transmetallation reaction.⁴⁷ Thus 21 was treated with phenyllithium in Et_2O at -78°C for 1 h to effect the generation of a vinyl anion, (eq.22). Addition of iodomethane to



such a solution resulted in the isolation of the sulfur-methylated product, 5, in 63% yield along with 50% yield of Ph_4Sn . It is clear that the transmetallation should have produced anion 20; however, since methylation occurred at sulfur, 20 must have been able to convert to the sulfur anion species.

After finding that the MeHg-derivative 17 could be isomerized to the dithiolene complex 18, it was wondered whether the same type of transformation occurs when the Group IVA metal halides are added to the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ system. From these reactions only the metallated dithiolene products had been isolated, eq.18. However, it was possible to isolate two sulfur-metallated compounds, 22 and 23, when the reactions were carried out using diethyl ether as the solvent, (eq.23).



The $\text{PhC}\equiv\text{CLi}$ was generated in Et_2O and $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ was added to these solutions at -78°C . The mixtures became brown and after 30 min the triphenylmetal halides were added (Ph_3SnCl , Ph_3PbBr). The reaction mixtures became red and a white precipitate (LiX , $\text{X} = \text{Cl}, \text{Br}$) formed during a 30 min period at -78°C . The solutions were allowed to warm to room temperature prior to removal of the solvents, but this did not affect the initially formed products, 22 and 23, which then were isolated. Compounds 22 and 23 are the first Group IVA metal derivatives of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ isolated, with a metal-sulfur bond, in which the metal atom does not bridge the two sulfur atoms. In fact,

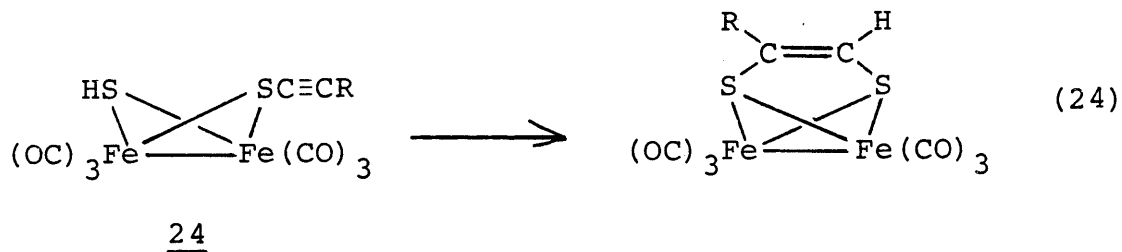
only mercury derivatives of $(\mu-S_2)Fe_2(CO)_6$ have been reported to form stable metal complexes of this sort.⁴⁸ Complex 22, however, could not be chromatographed, decomposing on both silica and alumina supports. It was, instead, crystallized in 26% yield from a pentane solution of the reaction residue after removal of the diethyl ether. The Ph_3Pb -derivative was less sensitive and was isolated in 71% yield as a red, glassy solid after filtration chromatography (silicic acid, eluting with a 9/1, v/v pentane/ CH_2Cl_2 mixture). Both compounds were reasonably air-stable and could be handled on the bench without special precautions. Identification of 22 and 23 as the sulfur metallated products was possible by the observance of a $\nu(C\equiv C)$ band in the IR spectra of each (2172 and 2175 cm^{-1} , respectively) and two alkyne carbon signals for each in their ^{13}C NMR spectra (δ_C 86.6, 86.9 and δ_C 86.1, 87.0, respectively). These carbon shifts compare well with those of the other unbridged phenylacetylene derivatives which occur in the region δ_C 93.4 to 82.2.

Having isolated these compounds, experiments were conducted to see if they would isomerize to the corresponding dithiolene complexes. Like the open mercury derivative 17, 23 was stable in THF solution being reisolated in 97% yield after 18 h. When 23 was added to a $-78^\circ C$ THF solution containing an equivalent of LiBr, the mixture became brown. After the solution was stirred for 2 h at $-78^\circ C$ and 3 h at room temperature, TLC analysis of the reaction mixture indicated that all of 23 had decomposed. Only the pentane soluble product, 7a

was isolated in 26% yield. There was never any evidence for the formation of the Ph_3Pb -dithiolene compound. Repeating the reaction in the presence of two equivalents of Ph_3PbBr gave the same results; 7a was isolated in 27% yield. Exactly how 7a forms in these reactions is not clear, but it was again the only isolable product when 22 was added to a LiCl/THF solution which was stirred at -78°C for 30 min and at room temperature for 4 h. Although these reactions failed to give the expected dithiolene products, they did show that 22 and 23 are unstable under the reaction conditions used to synthesize their corresponding dithiolene isomers, eq.18. These results support the conclusion that the Group IVA metal dithiolene compounds are formed not by isomerization of an initially formed sulfur-quenched product, but rather by direct reaction of the metal halide with carbanion intermediates.

All of the results involving the use of aldehydes and MeHgCl as electrophiles and the transmetallation reaction strongly suggest that thiolate and vinyl carbanion intermediates existing in equilibrium are involved in the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{-Fe}_2(\text{CO})_6$ reaction mixtures. With such an equilibrium the type of product obtained, cyclized or open, depends on 1) rate of reaction with the two intermediates and 2) reversible reaction with the sulfur anion. In the case of alkyl halides and acid chlorides, dithiolene ligand formation apparently is precluded due to a much faster reaction with the sulfur anion intermediate. As shown experimentally, MeHgCl reacts at sulfur first, before conversion to the dithiolene complex, a conversion which

no doubt depends on reversible addition to sulfur. Protonation of the $\text{RC}\equiv\text{CLi}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction mixture at -78°C probably gives complexes of type 24 which could isomerize by intramolecular thiol addition to the alkyne, (eq.24).



Experimental Section

General Comments

All reactions were carried out under an atmosphere of pre-purified tank nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Diethyl ether was distilled from lithium aluminum hydride. Reagent grade pentane, dichloromethane, and absolute ethanol were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Acetylene was pretreated by passing it through a -78°C trap, bubbling through concentrated sulfuric acid and then passing it through a column of activated alumina (MCB, 8-14 mesh). Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 ml) in a 350 ml glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration. Column chromatographies were performed with a 350 x 25 mm column using either silicic acid or Florisil (Fisher, 100-200 mesh). All chromatography was done without exclusion of atmospheric oxygen or moisture; all solid products were recrystallized from deoxygenated solvents at -20°C .

Infrared spectra were obtained using a Perkin Elmer Model 457A or Model 283 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60, JeolFX-90Q or Bruker 250 NMR spectrometers operating at 60MHz, 90MHz and 250MHz, respectively. ^{13}C NMR spectra were obtained using a JeolFX-90Q or Bruker 270

instrument operating at 22.5MHz and 67.9MHz, respectively. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70eV. Melting points were determined on analytically pure samples using a Buchi Capillary Melting Point Apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Lithium diisopropylamide was prepared just prior to use by adding one equivalent of *n*-butyllithium (Alfa) to a THF solution of diisopropylamine at 0°C then stirring at room temperature for 1 h. (μ -Dithio)bis(tricarbonyliron) was prepared as described in the literature.²³ Isomer ratios of the (μ -RS)(μ -R'S)Fe₂(CO)₆ type complexes were determined by integration of the appropriate signals in the ¹H NMR spectrum. Isomer ratios of solid products were obtained from recrystallized samples.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Cyclopentylmagnesium Bromide and Iodomethane. (GBW-I-56).

A 300 ml, three-necked, round-bottomed flask equipped with serum caps and a magnetic stir-bar was charged with 1.0 g (2.91 mmol) of (μ -S₂)Fe₂(CO)₆ and flushed with nitrogen. THF (75 ml) was added by syringe and a red solution was obtained. The solution was cooled to -78°C, whereupon 12 ml (7.9 mmol) of a 0.66M THF solution of cyclopentylmagnesium bromide was added. The solution then became green and was stirred for 15 min before 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture then was stirred for 30 min at -78°C and 2.5 h at room temperature during which time it became

red. The solvent was removed, leaving a red oil, which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands which were collected together. Removal of the solvent yielded 1.14 g (2.67 mmol, 91% yield) of $(\mu\text{-cyclo-C}_5\text{H}_9\text{S})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a slightly air sensitive red oil. After short path distillation (120°C, 0.2 mmHg), it was identified as a mixture of three isomers, the ratio of which could not be determined due to overlap of the SCH_3 and cyclopentyl proton signals.

IR (CHCl_3): 2980(s), 2890(m), 1449(m), 1431(m), 1321(m), 1312(m), 1246(m), 1127(m), 950(w), 830(m), 570(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2083(s), 2050(vs), 1994(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.62 (a), 2.08 (e), 2.12 (e) (all s, 3H, -SMe), 2.81 (m) and 1.4 to 1.9 (m, 9H, cyclopentyl ring).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_2$: C, 33.67; H, 2.83%.

Found: C, 33.82; H, 2.91%.

Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Isobutylmagnesium Bromide and Iodomethane. (GBW-II-11).

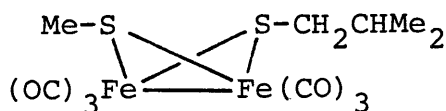
Following the procedure outlined on p. 55, 0.72 g (2.1 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 75 ml of THF was treated with 2.75 ml (2.7 mmol) of a 0.98M THF solution of isobutylmagnesium bromide at -78°C. The solution became green and was stirred for 15 min before 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was then stirred for 30 min at -78°C and 2 h at room temperature during which time it became

red. The solvent was removed leaving a red oil which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands which were collected together. Removal of the solvent yielded 0.86 g (2.07 mmol, 99% yield) of $(\mu\text{-Me}_2\text{CHCH}_2\text{S})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil. After short path distillation (130°C, 0.5 mmHg) it was identified as a mixture of three isomers based on the following data:

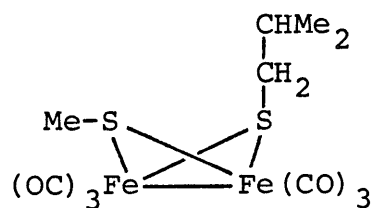
IR (CHCl_3): 2980(m), 2950(m), 2890(m), 1466(m), 1426(w), 1419(w), 1385(w), 1369(m), 1316(m), 618(s), 563(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2083(s), 2053(vs), 1993(vs) cm^{-1} .

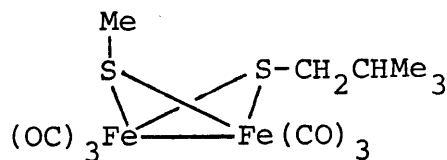
^1H NMR (CDCl_3 , 250MHz): δ 1.64 (a,e), 2.10 (e,e), 2.11 (e,a) (all s, 3H, SCH_3), 1.95 (d, $J = 7.0\text{Hz}$, SCH_2 , e,a), 2.32 (e,e) and 2.33 (a,e) (d, $J = 6.6\text{Hz}$, SCH_2), 0.93 (a,e), 1.03 (e,e) and 1.08 (e,a) (all d, $J = 6.6\text{Hz}$, $\text{CH}(\text{CH}_3)_2$), 1.91 to 1.77 and 1.58 to 1.52 (m, 1H, CH).



e,e



e,a



a,e

Isomer ratio: e,e/e,a/a,e = 2.5/1/3.3.

Anal. Calcd. for $C_{11}H_{12}Fe_2O_6S_2$: C, 31.76; H, 2.91%.

Found: C, 31.81; H, 2.94%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Cyclopropylmagnesium Bromide and Iodomethane. (GBW-I-63).

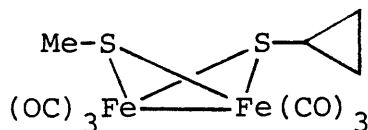
Following the procedure outlined on p. 55, 0.92 g (2.68 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 75 ml of THF was treated with 15 ml (7.0 mmol) of a 0.47M THF solution of cyclopropylmagnesium bromide at $-78^\circ C$. The solution became green and was stirred for 15 min before 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was then stirred for 30 min at $-78^\circ C$ and 3 h at room temperature during which time it became red. The solvent was removed leaving a red oil which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands which were collected together. Removal of the solvent yielded 1.04 g (2.46 mmol, 92% yield) of $(\mu\text{-cyclo-C}_3\text{H}_5\text{S})(\mu\text{-MeS})Fe_2(CO)_6$ as an air-stable, red solid. After recrystallization from pentane, mp $63\text{-}68^\circ C$, it was identified on the basis of the following data:

IR ($CHCl_3$): 3025(m), 2940(m), 2840(w), 1431(m), 1318(m), 1288(m), 1200(m), 1060(w), 1033(m), 955(m), 934(w), 885(m), 620(s), 575(s) cm^{-1} ;

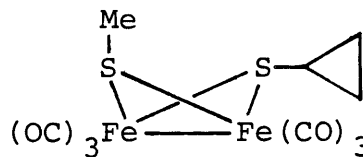
terminal carbonyl region ($CHCl_3$): 2090(s), 2060(vs), 2000(vs) cm^{-1} .

1H NMR ($CDCl_3$, 250MHz): δ 1.54 (a), 2.07 (e) (s, 3H, SCH_3), 1.74 to 1.62 (m, 1H, SCH), 0.86 to 0.70 and 1.14 to 1.0 (m,

4H, ring protons).



e,e



a,e

Isomer ratio: e,e/a,e = 1/1.

Anal. Calcd. for $C_{10}H_8Fe_2O_6S_2$: C, 30.03; H, 2.02%.

Found: C, 30.25; H, 2.10%.

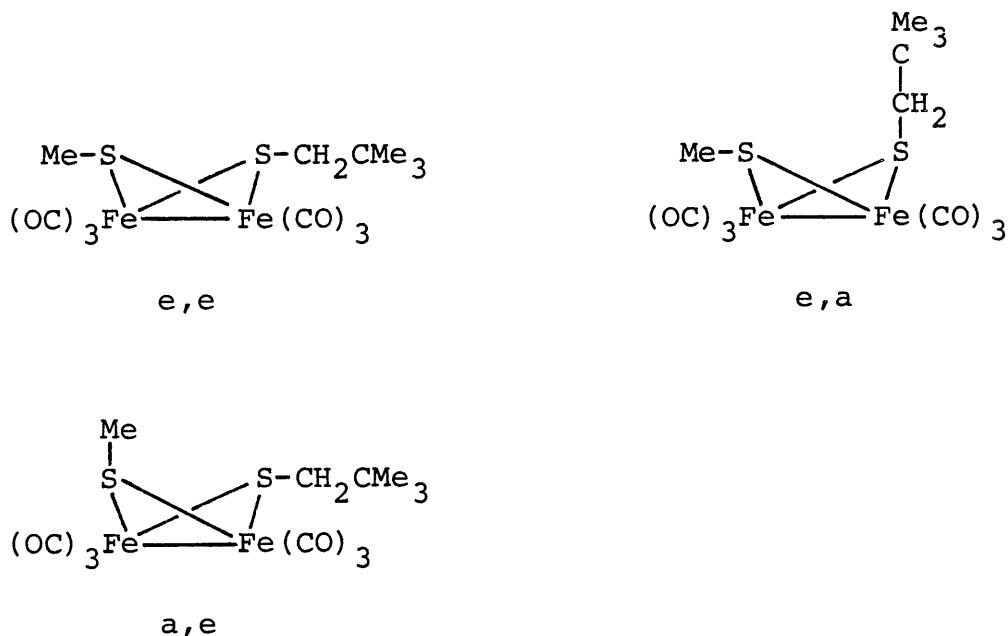
Reaction Between (μ -Dithio)bis(tricarbonyliron), Neopentylmagnesium Chloride and Iodomethane. (GBW-II-4).

Following the procedure outlined on p. 55, 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 75 ml of THF was treated with 4.78 ml (10.8 mmol) of a 2.27M diethyl ether solution of neopentylmagnesium chloride at $-78^\circ C$. The solution became green and was stirred for 15 min before 1.0 (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was then stirred for 30 min at $-78^\circ C$ and 3 h at room temperature during which time it became red. The solvent was removed leaving a red oil which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands which were collected together. Removal of the solvent yielded 0.54 g (1.26 mmol, 43% yield) of $(\mu-Me_3CCH_2S)(\mu-MeS)Fe_2(CO)_6$ as a slightly air-sensitive red oil. After short path distillation ($112^\circ C$, 0.24 mmHg) it was identified based on the following data:

IR (CHCl_3): 2975(s), 2945(m), 2920(m), 2885(m), 1470(m), 1430(w), 1398(m), 1375(s), 1323(m), 1311(w), 1273(m), 1245(w), 1188(w), 954(m), 908(m), 640(s), 565(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2089(s), 2055(vs), 2000(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.93 (e,a), 1.03 (e,e), 1.09 (a,e) (s, 9H, CMe_3), 2.10 (e,e and e,a), 1.66 (a,e) (s, 3H, SCH_3), 1.99 (e,a), 2.36 (e,e) and 2.35 (a,e) (s, 2H, SCH_2).



Isomer ratio: e,e/e,a/a,e = 1.3/1/1.3.

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{Fe}_2\text{O}_6\text{S}_2$: C, 33.52; H, 3.28%.

Found: C, 33.81; H, 3.41%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), *para*-Tolylmagnesium Bromide and Iodomethane. (GBW-II-13).

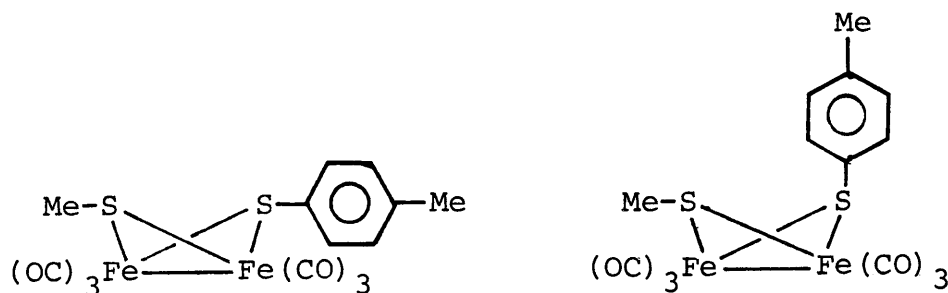
Following the procedure outlined on p.55, 0.85 g (2.47 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 75 ml of THF was treated with 3.40 ml

(3.60 mmol) of a 1.06M THF solution of para-tolylmagnesium bromide at -78°C . The solution became green and was stirred for 15 min before 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was then stirred for 30 min at -78°C and 3 h at room temperature during which time it became red. The solvent was removed leaving a red oil which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.98 g (2.19 mmol, 89% yield) of $(\mu\text{-p-MeC}_6\text{H}_4\text{S})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After recrystallization from pentane, mp $106\text{-}108^{\circ}\text{C}$, it was identified based on the following data:

IR (CHCl_3): 3010(m), 2940(m), 2878(w), 1655(w), 1605(w), 1561(w), 1490(m), 1429(m), 1397(w), 1318(m), 1306(m), 1179(m), 1122(m), 1019(m), 955(m), 907(m), $570(\text{s})\text{ cm}^{-1}$;

terminal carbonyl region (CHCl_3): 2090(s), 2055(vs), 2000(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 2.05, 2.15 and 2.17 (s, 6H, methyl groups), 6.9 to 7.1 (m, 4H, Ph).



Two isomers present in a ratio of 4/1 determined by integration of the signals at δ 2.05 and 2.15, but assignment of signals to either isomer could not be made.

Anal. Calcd. for $C_{14}H_{10}Fe_2O_6S_2$: C, 37.37; H, 2.24%.

Found: C, 37.39; H, 2.33%.

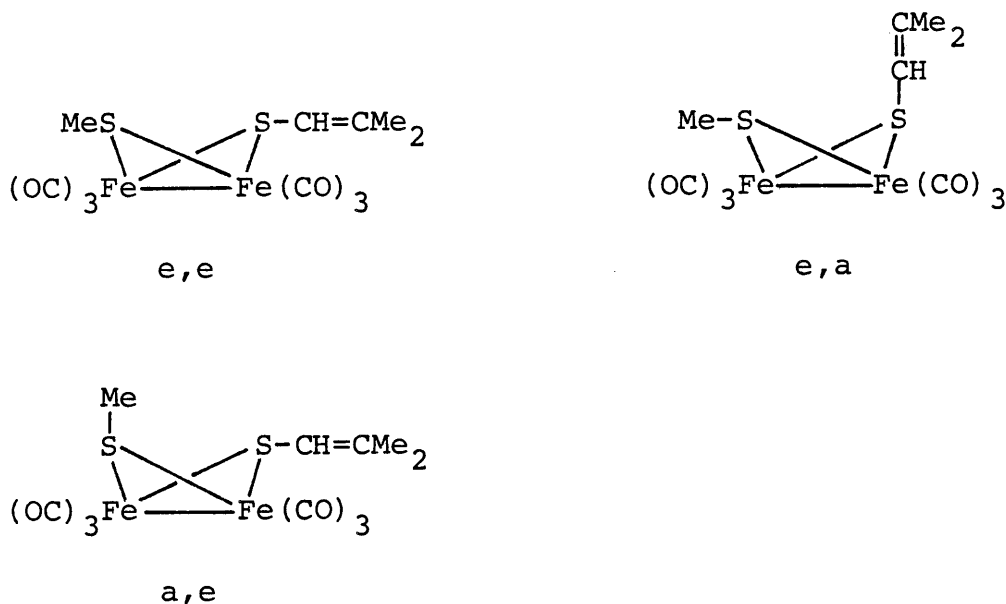
Reaction Between (μ -Dithio)bis(tricarbonyliron), Isobutenylmagnesium Bromide and Iodomethane. (GBW-II-15, I-68).

Following the procedure outlined on p. 55, 0.85 g (2.47 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 75 ml of THF was treated with 3.55 ml (2.95 mmol) by a 0.83M THF solution of isobutenylmagnesium bromide at $-78^\circ C$. The solution became green and was stirred for 15 min before 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was then stirred for 30 min at $-78^\circ C$ and 2 h at room temperature during which time it became red. The solvent was removed leaving a red oil which was taken up in pentane and applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.96 g (2.32 mmol, 94% yield) of $(\mu-Me_2C=CHS)-(\mu-MeS)Fe_2(CO)_6$ as a slightly air-sensitive red oil. After short path distillation ($85^\circ C$, 0.06 mmHg) it was identified based on the following data:

IR ($CHCl_3$): 3020(w), 2990(w), 2930(m), 2870(w), 1620(w) (C=C), 1434(m), 1380(m), 1320(m), 1180(w), 955(w), 933(w), 620(s), 570(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2090(s), 2058(vs), 2000(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.66 (a,e), 2.09 (e,e), 2.12 (e,a) (s, 3H, SCH_3), 1.98, 1.79 (a,e), 1.89, 1.76 (e,e), 1.83, 1.70 (e,a) (all s, 6H, $=\text{CMe}_2$), 5.40 (e,a), 5.54 (e,e), 5.62 (a,e) (s, 1H, vinyl proton).



Isomer ratio: $e,e/e,a/a,e = 1.6/1/1.9$.

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2$: C, 31.91; H, 2.43%.

Found: C, 31.90; H, 2.45%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-hexyne and Iodomethane. (GBW-V-63).

A dry, three-necked, 300 ml round-bottomed flask equipped with serum caps and a magnetic stir-bar was flushed with nitrogen and charged with 40 ml of THF and 0.41 ml (3.50 mmol) of 1-hexyne (Aldrich). This was cooled to -78°C and 1.59 ml (3.50 mmol) of a 2.2M n-butyllithium in hexane solution (Alfa) was added by syringe. The mixture then was removed from the

cold bath and stirred for 1 h to form the 1-lithio-1-hexyne. The reagent solution then was cooled to -78°C , and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ dissolved in 10 ml of THF was cannulated into it, resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 2.0 ml (32.1 mmol) of iodomethane (Aldrich) was added by syringe. The solution was stirred for 30 min at -78°C and 1 h at room temperature during which time a color change of green-to-red occurred. The solvent was removed on a rotary evaporator leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded, after removal of solvent, 1.19 g (2.70 mmol, 93% yield) of $(\mu\text{-C}_4\text{H}_9\text{C}\equiv\text{CS})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil, identified as a mixture of two isomers the ratio of which could not be determined due to overlapping CH_3 and n-butyl proton signals.

IR (CHCl_3): 2970(s), 2843(s), 2887(m), 2201(m) ($\text{C}\equiv\text{C}$), 1470(m), 1428(m), 1381(m), 1367(w), 1320(m), 1260(w), 1110(m), 957(m), 901(w), 870(w), 560(s) cm^{-1} ;

terminal carbonyl region: 2080(s), 2048(vs), 2000(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.84, 1.30 and 2.10 (all complex multiplets).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 8.4 (q, $J = 141\text{Hz}$, $-\text{CH}_3$), 13.4 (q, $J = 126\text{Hz}$, $-\text{CH}_3$), 19.6 (t, $J = 133\text{Hz}$, $-\text{CH}_2$), 21.9 (t, $J = 130\text{Hz}$, CH_2), 30.3 (t, $J = 121\text{Hz}$, CH_2), 70.8, 73.1, 91.4, 92.2 (all s, alkynyl carbons), 208.0 and 208.9 (both s, CO).

Anal. Calcd. for $C_{13}H_{12}Fe_2O_6S_2$: C, 35.48; H, 2.75%.

Found: C, 35.63; H, 2.84%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Iodomethane. (GBW-V-65, LCS-II-18).

Using the standard reaction vessel and procedure (p. 63) 3.19 mmol of $LiC\equiv CPh$ was generated in 40 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This reagent solution was cooled to $-78^\circ C$ and 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at $-78^\circ C$, then 1.5 ml (24.1 mmol) of iodomethane was added. The reaction mixture was stirred for 1 h at $-78^\circ C$ and 1 h at room temperature during which time the solution became red. The solvent was removed, leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after removal of solvent yielded 1.13 g (2.46 mmol, 85% yield) of $(\mu-PhC\equiv CS)(\mu-MeS)Fe_2(CO)_6$ as an air-stable red solid. After recrystallization from pentane, mp $80-100^\circ C$ (dec), it was identified as a mixture of two isomers, 1.3/1 (CH_3 a/ CH_3 e).

IR ($CHCl_3$): 2937(w), 2193(m) ($C\equiv C$), 1599(m), 1577(m), 1492(m), 1448(m), 1320(m), 1313(m), 1072(w), 1031(w), 957(m), 867(m), 615(s), 555(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2085(s), 2051(vs), 2000(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 270MHz): δ 1.63 (s, CH_3 , a), 2.15 (s, CH_3 , e) and 7.38 (m, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 8.7 (q, $J = 141\text{Hz}$, CH_3), 19.6 (q, $J = 141\text{Hz}$, CH_3), 82.2, 84.3, 88.1, 88.9 (all s, alkynyl), 122.2 (t, $^2J = 8\text{Hz}$, ipso Ph), 128.3 (d, $J = 162\text{Hz}$, Ph), 129.0 (d, $J = 163\text{Hz}$, Ph), 132.0 (d, $J = 161\text{Hz}$, Ph), 208.7 and 207.8 (both s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2$: C, 39.16; H, 1.75%.

Found: C, 39.16; H, 1.89%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Iodoethane. (GBW-X-58, LCS-II-22).

Using the standard procedure (p. 63), 1.55 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.18 ml (1.60 mmol) of phenylacetylene and 0.63 ml (1.55 mmol) of a 2.48M n-butyllithium solution. This was cooled to -78°C and 0.5 g (1.46 mmol) of ($\mu\text{-S}_2$) $\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 15 min at -78°C , 1.0 ml (12.5 mmol) of iodoethane (Aldrich) was added. The reaction mixture was stirred for 30 min at -78°C and 2 h at room temperature. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which gave 0.52 g (1.10 mmol, 75% yield) of ($\mu\text{-EtS}$)($\mu\text{-PhC}\equiv\text{CS}$) $\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil, identified as a mixture of three isomers; 3/1.7/1 (Et a/Et e/Et e).

IR (CHCl_3): 2985(w), 2959(m), 2897(w), 2182(m) ($\text{C}\equiv\text{C}$), 1602(w), 1496(m), 1452(m), 1385(w), 1262(m), 620(s), 571(s) cm^{-1} ;

terminal carbonyl region: 2079(s), 2044(vs), 1996(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.16 (t, $J = 7.4\text{Hz}$, CH_3 a), 1.35 (t, $J = 7.4\text{Hz}$, CH_3 e), 1.46 (t, $J = 7.2\text{Hz}$, CH_3 e), 2.04 (q, $J = 7.4\text{Hz}$, CH_2 a), 2.49 (q, $J = 7.4\text{Hz}$, CH_2 e), 2.81 (q, $J = 7.2\text{Hz}$, CH_2 e), 7.2 to 7.5 (m, Ph).

^{13}C $\{^1\text{H}\}$ (CD_2Cl_2 , 67.9Hz): δ_{C} 19.4, 22.0, 22.5, 24.9, 36.9, 38.5 (Et), 89.4, 92.6, 93.4 (alkynyl), 127.1, 129.9, 132.8, 133.3, 133.6, 133.9, 136.1, 136.8, 139.5 (Ph), 212.6, 213.0, 213.8 (CO).

Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2$: C, 40.54; H, 2.13%.

Found: C, 40.68; H, 2.27%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Benzyl Chloride. (GBW-X-59, LCS-II-25).

Using the standard procedure (p. 63), 1.55 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.18 ml (1.60 mmol) phenylacetylene and 0.63 ml (1.55 mmol) of a 2.48M n-butyllithium solution. This was cooled to -78°C and 0.5 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 15 min at -78°C , 0.70 ml (6.0 mmol) of benzyl chloride (Aldrich) was added. The reaction mixture was stirred for 30 min at -78°C and 4 h at room temperature. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted

a minor red band which yielded a red oil identified as a mixture of benzyl chloride and $(\mu\text{-SCH}=\text{C}(\text{Ph})\text{S})\text{Fe}_2(\text{CO})_6$ by ^1H NMR. Pentane/ CH_2Cl_2 (9/1, v/v) eluted a second red band which gave 0.22 g (0.41 mmol, 28% yield) of $(\mu\text{-PhCH}_2\text{S})(\mu\text{-PhC}\equiv\text{C}(\text{S})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid, mp 122-125°C after recrystallization from pentane/ CH_2Cl_2 , identified as a mixture of two isomers, 9/1 (PhCH_2 a/ PhCH_2 e).

IR (CHCl_3): 2190(m) ($\text{C}\equiv\text{C}$), 1604(w), 1498(m), 1464(m), 1453(m), 1081(m), 872(m), 628(s), 573(s) cm^{-1} ;

terminal carbonyl region: 2078(s), 2044(vs), 2006(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 3.19 (s, CH_2 a), 3.62 (s, CH_2 e), 7.0 to 7.6 (m, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 67.9MHz): δ_{C} 29.4 (CH_2 a), 41.2 (CH_2 e), 89.0, 84.3 (alkynyl), 122.2, 127.8, 128.4, 128.8, 129.1, 129.2, 132.1, 138.1 (Ph), 207.7 and 208.8 (CO).

Anal. Calcd. for $\text{C}_{21}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_5$: C, 47.05; H, 2.26%.

Found: C, 47.28; H, 2.40%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and 1-Bromo-2-propanone. (GBW-X-57).

Using the standard procedure (p. 63), 1.55 mmol of $\text{PhC}\equiv\text{CLi}$ was generated in 40 ml of THF from 0.18 ml (1.60 mmol) of $\text{PhC}\equiv\text{CH}$ and 0.63 ml (1.55 mmol) of a 2.48M n-butyllithium solution. This was cooled to -78°C and 0.5 g (1.46 mmol) of $(\mu\text{-S}_2)\text{-Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 15 min at -78°C ,

0.41 g (3.0 mmol) of $\text{BrCH}_2\text{C}(\text{O})\text{CH}_3$ was added causing a color change to red. The solution was removed from the cold bath and stirred for 1 h. Subsequently, the solvent was removed and the remaining red tar subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 0.55 g (1.10 mmol, 75% yield) of $(\mu\text{-MeC}(\text{O})\text{CH}_2\text{S})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid, mp 88-91°C after crystallization from pentane/ CH_2Cl_2 , identified as a mixture of two isomers by ^1H NMR spectroscopy; 13/1 ($\text{CH}_3\text{C}(\text{O})\text{CH}_2$ a/ $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ e).

IR (CHCl_3): 2174(m) ($\text{C}\equiv\text{C}$), 1713(s) ($\text{C}=\text{O}$), 1598(w), 1576(w), 1490(m), 1444(w), 1380(w), 1360(m), 1268(w), 1147(m), 1069(w), 1027(w), 861(m), 688(m), 613(s), 563(s), 480(s) cm^{-1} ;

terminal carbonyl region: 2084(s), 2047(vs), 2011(vs), 1999(sh) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 2.22 (s, CH_3 a), 2.28 (s, CH_3 e), 2.79 (s, CH_2 a), 3.33 (s, CH_2 e) and 7.5-7.1 (m, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 67.9MHz): δ_{C} 29.2 (CH_3 a), 34.3 (CH_3 e), 46.6 (CH_2 a), 48.5 (CH_2 e), 83.4, 89.5 (alkynyl), 122.0, 128.4, 129.2, 132.1 (Ph); 201.9 (ketone CO), 207.3 and 208.4 (CO).

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{Fe}_2\text{O}_7\text{S}_2$: C, 40.67; H, 2.01%.

Found: C, 40.86; H, 2.19%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 4-Lithio-2-methyl-1-buten-3-yne and Iodomethane. (GBW-X-42).

Using the standard reaction vessel and procedure (p. 63),

3.50 mmol of $\text{LiC}\equiv\text{CC}(\text{Me})=\text{CH}_2$ was generated in 50 ml of THF from 0.34 ml (3.50 mmol) of 2-methyl-1-buten-3-yne (Farchan) and 1.42 ml (3.50 mmol) of a 2.47M n-butyllithium solution. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 15 min at -78°C , then 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction mixture was stirred for 15 min at -78°C and 1 h at room temperature. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 1.12 g (2.64 mmol, 91% yield) of $(\mu\text{-CH}_2=\text{C}(\text{Me})\text{C}\equiv\text{CS})(\mu\text{-MeS})\text{-Fe}_2(\text{CO})_6$ as an air-stable red solid. After crystallization from pentane, mp $83\text{-}90^\circ\text{C}$, it was identified as a mixture of two isomers, 5/1 (CH_3 e/ CH_3 a).

IR (CHCl_3): 3000(w), 2966(w), 2935(m), 2840(w), 1161(m) (C=C), 1454(m), 1428(m), 1374(m), 1316(m), 1279(m), 1016(w), 992(w), 955(m), 904(s), 868(w), 613(s), 565(s), 480(s) cm^{-1} ;

terminal carbonyl region: 2077(s), 2041(vs), 2008(vs), 1998(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.54 (SCH_3 a), 1.80 (CH_3), 2.09 (SCH_3 e), 5.26 and 5.32 (both s, vinyl).

^{13}C $\{^1\text{H}\}$ NMR (C_6D_6), 67.9MHz): δ_{C} 8.39 (SCH_3 a), 18.9 (SCH_3 e), 22.6, 21.3 (CH_3), 81.5, 90.0 (alkynyl), 123.8, 124.4, 126.5 (vinyl), 208.2 and 209.1 (CO).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2$: C, 33.99; H, 1.93%.

Found: C, 34.13; H, 2.00%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-heptyne and Iodomethane. (GBW-X-50).

Using the standard procedure (p. 63), 1.60 mmol of $n\text{-C}_5\text{H}_{11}\text{C}\equiv\text{CLi}$ was generated in 40 ml of THF from 0.17 g (1.76 mmol) of 1-heptyne (Aldrich) and 0.65 ml (1.60 mmol) of a 2.47M n -butyllithium solution. This was cooled to -78°C and 0.50 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it, resulting in a green reaction mixture. After stirring for 15 min at -78°C , 0.50 ml (8.0 mmol) of MeI (Aldrich) was added. The solution was stirred for 10 min at -78°C and 1 h at room temperature during which time it became red. The solvent was removed and the remaining red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.59 g (1.30 mmol, 89% yield) of $(\mu\text{-n-C}_5\text{H}_{11}\text{C}\equiv\text{CS})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified as a mixture of three isomers; the isomer ratio of which could not be determined due to overlapping CH_3 and pentyl signals.

IR (CHCl_3): 2964(s), 2938(s), 2867(s), 2190(m) ($\text{C}\equiv\text{C}$), 1466(m), 1428(m), 1381(w), 1369(w), 1348(w), 1327(m), 1317(m), 953(m), 615(s), 570(s), 480(s) cm^{-1} ;

terminal carbonyl region: 2077(s), 2038(vs), 2002(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.86, 1.32 and 2.19 (all multiplets), 1.52 (s, CH_3 a) and 2.07 (s, CH_3 e).

^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 67.9MHz): δ_{C} 8.1, 14.0, 19.2, 20.0, 20.2, 21.5, 22.4, 24.3, 28.2, 29.5, 30.1, 31.2 (SCH_3 and n -pentyl),

64.6, 71.3, 73.6, 90.4, 91.9, 92.7 (alkynyl), 208.4 and 209.3 (CO).

Anal. Calcd. for $C_{14}H_{14}Fe_2O_6S_2$: C, 37.03; H, 3.11%.

Found: C, ; H, %.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-heptyne and 1-Bromo-2-propanone. (GBW-X-53).

Using the standard procedure, 1.60 mmol of $n-C_5H_{11}C\equiv CLi$ was generated in 40 ml of THF from 0.17 g (1.76 mmol) of 1-heptyne and 0.65 ml (1.60 mmol) of a 2.47M n-butyllithium solution. This was cooled to $-78^\circ C$ and 0.50 g (1.46 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it, resulting in a green reaction mixture. After stirring for 15 min at $-78^\circ C$, 0.41 g (3.0 mmol) of $BrCH_2C(O)CH_3$ was added causing a color change to red. The solution was removed from the cold bath and stirred for 1 h. Subsequently, the solvent was removed and the remaining red tar subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which yielded 0.56 g (1.12 mmol, 77% yield) of $(\mu-MeC(O)CH_2S)(\mu-n-C_5H_{11}C\equiv CS)Fe_2(CO)_6$ as a slightly air-sensitive red oil, identified as a mixture of three isomers; 2.7/1/0.3 ($MeC(O)CH_2$ a/ $MeC(O)CH_2$ e/ $MeC(O)CH_2$ e).

IR ($CHCl_3$): 2967(m), 2940(s), 2869(m), 2190(m) ($C\equiv C$), 1715(s) ($C=O$), 1460(m), 1380(w), 1359(m), 1326(w), 1147(m), 613(s), 565(s) cm^{-1} ;

terminal carbonyl region: 2079(s), 2043(vs), 2005(vs), 1997(sh) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.84, 1.30 (both m, pentyl), 2.16 (s, CH_3 a), 2.23 (s, CH_3 e), 2.30 (s, CH_3 e), 2.71 (CH_2 a), 3.25 (CH_2 e) and 3.35 (CH_2 e).

^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 67.9MHz): δ 13.9, 20.0, 22.3, 28.2, 28.5, 31.2, 33.8, 46.3 (pentyl, CH_2 and CH_3), 70.9, 72.9, 92.4, 93.2, (alkynyl), 199.5, 200.3 (ketone CO), 208.1 and 209.1 (CO).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{Fe}_2\text{O}_7\text{S}_2$: C, 38.74; H, 3.25%.

Found: C, 38.84; H, 3.46%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium (Trimethylsilyl)acetylide⁵⁰ and Iodomethane. (GBW-X-47).

Using the standard reaction vessel and procedure (p. 63), 1.80 mmol of $\text{LiC}\equiv\text{CSiMe}_3$ was generated in 40 ml of THF from 0.21 g (2.14 mmol) of trimethylsilylacetylene and 0.73 ml (1.80 mmol) of a 2.47M n-butyllithium solution. This reagent solution was cooled to -78°C and 0.5 g (1.46 mmol) of (μ - S_2)- $\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 15 min at -78°C , 0.50 ml (8.0 mmol) of MeI (Aldrich) was added. The solution was stirred for 10 min at -78°C and 1 h at room temperature during which time a color change to red occurred. The solvent was removed leaving a red tar which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.57 g (1.25 mmol, 86% yield) of (μ - $\text{Me}_3\text{SiC}\equiv\text{CS}$)(μ -MeS) $\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After crystallization from pentane, mp 62 - 78°C , it was identified as a mixture of two isomers, 1.4/1 (CH_3 a/ CH_3 e).

IR (CHCl_3): 2970(m), 2935(w), 2909(w), 2108(s) ($\text{C}\equiv\text{C}$), 1456(w), 1428(m), 1410(m), 1317(m), 1250(s), 953(m), 865(s), 853(s), 615(s), 562(s), 481(s) cm^{-1} ;

terminal carbonyl region: 2079(s), 2048(vs), 2008(vs), 1967(w) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 2.08 (s, CH_3 e), 1.53 (s, CH_3 a) and 0.10 (s, SiCH_3).

^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 67.9MHz): δ_{C} -0.5 (SiCH_3), 8.4 (SCH_3 a), 1.90 (SCH_3 e), 96.7, 97.0, 97.4, 99.3 (alkynyl), 208.1 and 209.0 (CO).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_2\text{Si}$: C, 31.60; H, 2.65%.

Found: C, 31.50; H, 2.66%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium (Trimethylsilyl)acetylide⁵⁰ and Iodoethane. (GBW-X-52).

Using the standard procedure (p. 63), 1.80 mmol of $\text{LiC}\equiv\text{CSiMe}_3$ was generated in 40 ml of THF from 0.21 g (2.14 mmol) of trimethylsilylacetylene and 0.73 ml (1.80 mmol) of a 2.48M n-butyllithium solution. This was cooled to -78°C and 0.50 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 15 min at -78°C , 0.64 ml (8.0 mmol) of EtI (Aldrich) was added. The solution was stirred for 15 min at -78°C and 1 h at room temperature during which time it became red. The solvent was removed and the remaining red material subjected to filtration chromatography (silicic acid/pentane).

Pentane eluted a red band which yielded 0.58 g of $(\mu\text{-Me}_3\text{SiC}\equiv\text{CS})\text{-}(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After recrystallization from pentane, mp 90-92°C, it was identified as a mixture of two isomers, 3.2/1 (Et a/Et e).

IR (CHCl_3): 2975(m), 2939(m), 2911(w), 2880(w), 2100(s) ($\text{C}\equiv\text{C}$), 1460(m), 1416(w), 1385(w), 1257(s), 1053(w), 976(w), 873(s), 852(s), 620(s), 574(s), 490(s) cm^{-1} ;

terminal carbonyl region: 2080(s), 2042(vs), 2007(vs), 1998(sh) cm^{-1} .

^1H NMR (C_6D_6 , 250MHz): δ 0.08 (s, SiCH_3), 0.09 (s, SiCH_3), 0.63 (t, $J = 7.3\text{Hz}$, CH_3 a), 0.75 (t, $J = 7.4\text{Hz}$, CH_3 e), 1.42 (q, $J = 7.4\text{Hz}$, CH_2 a), 1.83 (q, $J = 7.3\text{Hz}$, CH_2 e).

^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 67.9Hz): δ_{C} -0.48 (SiCH_3), 17.1 (CH_3 a), 17.5 (Me e), 20.1 (CH_2 a), 31.9 (CH_2 e), 97.3, 99.3 (alkynyl), 208.3 and 209.1 (CO).

Anal. Calcd. for $\text{C}_9\text{H}_4\text{Fe}_2\text{O}_6\text{S}_2$: C, 33.21; H, 3.00%.

Found: C, 33.94; H, 3.02%.

Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Ethynylmagnesium Bromide⁴⁹ and Iodomethane. (GBW-X-48).

A dry 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar, serum caps and a gas dispersion tube was flushed with nitrogen. THF (50 ml) was added and acetylene (Airco) was bubbled into the solvent for 10 min. While continuing acetylene addition, 1.6 ml (3.61 mmol) of a 2.26M THF ethylmagnesium bromide solution was added by syringe. The

mixture acquired a pink tint and was stirred with continuous acetylene bubbling for another 20 min. The gas dispersion tube was removed, and the solution cooled to -78°C . In 10 ml of THF, 0.5 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ was then cannulated into the $\text{HC}\equiv\text{CMgBr}$ solution resulting in a brown reaction mixture. After stirring for 30 min at -78°C , 0.90 ml (14.4 mmol) of MeI (Aldrich) was added. Stirring was continued for 30 min at -78°C and 2 h at room temperature during which time the solution became red. The solvent was removed leaving a red tar which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.43 g (1.12 mmol, 77% yield) of $(\mu\text{-HC}\equiv\text{CS})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red solid. After crystallization from pentane, mp $95\text{-}100^{\circ}\text{C}$ dec, it was identified as a mixture of two isomers, 3/1 (CH_3 a/ CH_3 e).

IR (CHCl_3): 3309(s) ($\equiv\text{C-H}$), 3000(w), 2930(m), 2829(w), 1456(w), 1427(m), 1310(m), 954(m), 637(sh), 562(s), 480(s) cm^{-1} ;

terminal carbonyl region: 2078(s), 2040(vs), 2002(vs), 1997(sh) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 1.55 (s, CH_3 a), 2.09 (s, CH_3 e), 2.24 and 2.33 (both s, $\equiv\text{CH}$).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 9.2 (q, $J = 142\text{Hz}$, CH_3 a), 20.0 (q, $J = 141\text{Hz}$, CH_3 e), 76.2 (d, $J = 257\text{Hz}$, $\equiv\text{CH}$), 77.0 (d, $J = 257\text{Hz}$, $\equiv\text{CH}$), 78.8 (s, alkynyl), 208.2 and 209.1 (both s, CO).

Anal. Calcd. for $C_9H_4Fe_2O_6S_2$: C, 28.15; H, 1.05%.

Found: C, 28.35; H, 1.19%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Acetyl Chloride. (GBW-VI-15).

Using the standard reaction vessel and procedure (p.63), 3.19 mmol of $LiC\equiv CPh$ was generated in 50 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This reagent solution was cooled to $-78^\circ C$ and 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at $-78^\circ C$, then 2.07 ml (2.91 mmol) of acetyl chloride (Mallinckrodt) was added causing a color change to red. The reaction mixture was stirred for 15 min at $-78^\circ C$ and 45 min at room temperature. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which after removal of solvent yielded 1.31 g (2.69 mmol, 92% yield) of $(\mu-CH_3C(O)S)(\mu-PhC\equiv CS)-Fe_2(CO)_6$ as an air-stable red solid. After crystallization from pentane/ CH_2Cl_2 , mp $74-75^\circ C$ dec, it was identified based on the following data:

IR ($CHCl_3$): 3065(m), 2179(m) ($C\equiv C$), 1728(s) ($C=O$), 1598(m), 1574(w), 1489(m), 1446(m), 1417(w), 1354(s), 1097(s), 1033(m), 1004(m), 945(s), 867(m), 560(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2088(s), 2059(vs), 2021(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 2.40 (s, 3H, CH_3) and 7.34 (s, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 35.5 (q, $J = 131\text{Hz}$, CH_3), 84.0, 89.4 (both s, alkynyl), 122.1 (s, ipso Ph), 128.3 (d, $J = 156\text{Hz}$, Ph), 129.1 (d, $J = 154\text{Hz}$, Ph), 132.0 (d, $J = 162\text{Hz}$, Ph), 198.9 (s, organic CO) and 207.5 (s, CO).

Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{Fe}_2\text{O}_7\text{S}_2$: C, 39.38; H, 1.65%.

Found: C, 39.57; H, 1.84%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Pivaloyl Chloride. (GBW-VI-66).

Using the standard reaction vessel and procedure (p.63), 3.19 mmol of $\text{LiC}\equiv\text{CPh}$ was generated in 50 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 0.6 ml (5.0 mmol) of pivaloyl chloride (Eastman) was added causing a color change to red. The reaction mixture was stirred for 15 min at -78°C and 2 h at room temperature. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 1.03 g (1.94 mmol, 67% yield) of $(\mu\text{-Me}_3\text{CC}(\text{O})\text{S})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After crystallization from pentane/ CH_2Cl_2 , mp $80\text{-}82^\circ\text{C}$, it was identified based on the following data:

IR (CHCl_3): 2969(m), 2930(w), 2903(w), 2869(w), 2164(w) ($\text{C}\equiv\text{C}$), 1714(s) ($\text{C}=\text{O}$), 1688(m), 1594(w), 1581(w), 1484(m), 1473(m), 1457(m), 1440(w), 1393(w), 1364(m), 1067(w), 1038(m), 1034(m), 900(s), 885(m), 682(m), 608(s), 569(s), 550(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2076(s), 2042(vs), 2007(vs), cm^{-1} .

^1H NMR (acetone- d_6 , 90MHz): δ 1.28 (s, 9H, CH_3), 7.40 (s, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 28.0 (q, $J = 128\text{Hz}$, CH_3), 89.5 and 84.6 (both s, alkynyl), 122.1 (s, ipso Ph), 128.4 (d, $J = 162\text{Hz}$, Ph), 129.1 (d, $J = 161\text{Hz}$, Ph), 132.1 (d, $J = 163\text{Hz}$, Ph), 207.2 (s, organic CO) and 207.6 (s, CO).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{Fe}_2\text{O}_7\text{S}_2$: C, 43.05; H, 2.66%.

Found: C, 43.23; H, 2.81%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Iodomethane After Warming for 30 min. (GBW-VI-19).

Using the standard reaction vessel, 3.19 mmol of $\text{PhC}\equiv\text{CLi}$ was generated by the usual procedure (p. 63) and treated with 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ as before. The resulting green solution was stirred for 30 min at -78°C then removed from the cold bath and allowed to warm. As the solution warmed it became brown and after stirring for 30 min, 1.5 ml (24.2 mmol) of iodomethane was added. The solution became red and was stirred for 1 h. Subsequently, the solvent was removed and the remaining red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after

removal of solvent yielded 1.12 g (2.43 mmol, 84% yield) of $(\mu\text{-PhC}\equiv\text{CS})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison of its IR, ^1H NMR and ^{13}C NMR spectra to those of an authentic sample. An isomer ratio of 2/1 ($\text{CH}_3\text{ a}/\text{CH}_3\text{ e}$) was determined.

Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Lithium Phenylacetylide and Acetyl Chloride After Warming for 30 min.
(GBW-XI-15).

Using the standard reaction vessel, 1.56 mmol of $\text{PhC}\equiv\text{CLi}$ was generated by the usual procedure (p. 63) and treated with 0.5 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ as before. The resulting green solution was stirred for 30 min at -78°C then removed from the cold bath and allowed to warm. As the solution warmed it became brown and after stirring for 30 min, 0.5 ml (7.04 mmol) of acetyl chloride was added. The solution became red and was stirred for 1 h. Subsequently, the solvent was removed and the remaining red oil subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which after removal of solvent yielded 0.44 g (0.9 mmol, 62% yield) of $(\mu\text{-PhC}\equiv\text{CS})(\mu\text{-CH}_3\text{C(O)S})\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison of its IR and ^1H NMR spectra to those of an authentic sample.

Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Lithium Phenylacetylide and Iodomethane After Warming for 1.5 h. (GBW-XI-13).

Using the standard reaction vessel, 1.56 mmol of $\text{PhC}\equiv\text{CLi}$ was generated from 0.18 ml (1.60 mmol) of phenylacetylene

(Aldrich) and 0.63 ml (1.56 mmol) of a 2.49M n-butyllithium solution (p. 63). This reagent solution was treated with 0.5 g (1.46 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ as before. The resulting green solution was stirred for 30 min at -78°C then removed from the cold bath and allowed to warm. As the solution warmed it became brown and after stirring for 1.5 h, 1.0 ml (16.1 mmol) of iodomethane was added. After stirring for 1 h the solvent was removed and the remaining red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after removal of solvent yielded 0.22 g (0.48 mmol, 33% yield) of $(\mu\text{-PhC}\equiv\text{CS})(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6$ as a red solid, identified as one isomer (e Me) by comparison of its IR and ^1H NMR spectra to those of the authentic sample.

Reaction Between $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$, Lithium Phenylacetylide and Trifluoroacetic Acid. (GBW-III-72).

Lithium phenylacetylide, 6.96 mmol, was generated in 20 ml of THF from 0.80 ml (7.20 mmol) of phenylacetylene and 6.96 mmol of lithium diisopropylamide. This reagent solution was cannulated into a 300 ml, three-necked flask containing 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 50 ml of THF cooled to -78°C , producing a green reaction mixture which was stirred for 30 min at -78°C . Trifluoroacetic acid (Baker), 0.6 ml (8.08 mmol), was added causing an immediate color change to red. Stirring was continued at -78°C for 30 min, then at room temperature for 30 min prior to removal of the solvent. The remaining black solid was subjected to filtration chromatography (silicic acid/pentane); pentane eluting a red band which gave 1.17 g (2.53 mmol,

87% yield) of $(\mu\text{-SCH=C(Ph)S})\text{Fe}_2(\text{CO})_6$ as an air-stable dark red solid, mp 98-100°C dec (lit.³⁴ mp 95-97°C dec) after crystallization from pentane.

IR (CHCl_3): 3030(m, broad), 1483(m), 1440(m), 1175(m), 892(m), 613(m), 573(s), 550(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2078(s), 2043(vs), 2000(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 6.46 (s, 1H, =CH) and 7.30 (s, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 125.1 (d, $J = 166\text{Hz}$, Ph), 128.5 (d, $J = 162\text{Hz}$, Ph), 129.5 (d, $J = 161\text{Hz}$, Ph), 133.2 (s, ipso Ph), 134.4 (d, $J = 183\text{Hz}$, =CH), 166.7 (s, =CPh) and 207.5 (s, CO).

Mass spectrum, m/z (relative intensity): 418 ($\text{M}^+ - \text{CO}$, 4), 390 ($\text{M}^+ - 2\text{CO}$, 6), 362 ($\text{M}^+ - 3\text{CO}$, 4), 334 ($\text{M}^+ - 4\text{CO}$, 4), 306 ($\text{M}^+ - 5\text{CO}$, 8), 278 ($\text{M}^+ - 6\text{CO}$, 23), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 11), 112 (Fe_2 , 4), 88 (FeS , 3), 56 (Fe , 17).

Anal. Calcd. for $\text{C}_{14}\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$: C, 37.70; H, 1.36%.

Found: C, 37.66; H, 1.42%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 4-Lithio-2-methyl-1-buten-3-yne and Trifluoroacetic Acid. (GBW-III-74).

4-Lithio-2-methyl-1-buten-3-yne, 6.96 mmol, was generated in 20 ml of THF from 0.7 ml (7.20 mmol) of 2-methyl-1-buten-3-yne (Farchan) and 6.96 mmol of lithium diisopropylamide. This reagent solution was cannulated into a 300 ml, three-necked

flask containing 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ and 50 ml of THF cooled to $-78^\circ C$, producing a green reaction mixture which was stirred for 30 min. Subsequently, 0.6 ml (8.08 mmol) of trifluoroacetic acid (Baker) was added causing an immediate color change to red. Stirring was continued at $-78^\circ C$ for 10 min then at room temperature for 30 min prior to removal of the solvent. The black solid remaining was extracted with pentane until the extracts were colorless and the resulting red solution filtered. Removal of the solvent gave 1.06 g (2.59 mmol, 89% yield) of $(\mu-SCH=C(CMe=CH_2)S)Fe_2(CO)_6$ as an air-stable, dark red solid, mp $65.5-67^\circ C$ after crystallization from pentane.

IR ($CHCl_3$): 3095(m), 3040(w), 2953(m), 2926(m), 2858(m), 1600(m) (C=C), 1536(w), 1445(m), 1435(sh), 1370(m), 1290(w), 1182(m), 1020(m), 987(m), 904(s), 610(m), 555(m) cm^{-1} ;

terminal carbonyl region: 2078(s), 2043(vs), 2000(vs) cm^{-1} .

1H NMR ($CDCl_3$, 60MHz): δ 1.70 (s, 3H, CH_3), 5.16 (s, 1H, vinyl), 5.41 (s, 1H, vinyl), 6.09 (s, 1H, vinyl).

^{13}C NMR (CD_2Cl_2 , 67.9MHz): δ_C 21.3 (q, $J = 128Hz$, CH_3), 118.7 (t, $J = 159Hz$, $=CH_2$), 135.7 (d, $J = 183Hz$, $=C(H)S$), 138.5 (s, $=CMe$), 162.8 (s, $=CS$) and 208.3 (s, CO).

Mass spectrum, m/z (relative intensity): 382 (M^+-CO , 6), 354 (M^+-2CO , 9), 326 (M^+-3CO , 7), 298 (M^+-4CO , 6), 270 (M^+-5CO , 10), 242 (M^+-6CO , 29), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 5), 112 (Fe_2 , 3), 88 (FeS, 2), 56 (Fe, 14).

Anal. Calcd. for $C_{11}H_6Fe_2O_6S_2$: C, 32.23; H, 1.48%.

Found: C, 32.24; H, 1.59%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-hexyne and Trifluoroacetic Acid. (GBW-IV-12).

1-Lithio-1-heptyne, 6.0 mmol, was generated in 20 ml of THF from 0.81 ml (7.0 mmol) of 1-hexyne and 6.0 mmol of lithium diisopropylamide. This reagent solution was cannulated into a 300 ml, three-necked flask containing 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ and 50 ml of THF cooled to $-78^\circ C$, producing a green reaction mixture which was stirred for 30 min. Subsequently, 0.8 ml (10.8 mmol) of trifluoroacetic acid (Baker) was added causing an immediate color change to red. Stirring was continued at $-78^\circ C$ for 10 min then 30 min at room temperature prior to solvent removal. The remaining black tar was subjected to filtration chromatography (silicic acid/pentane); pentane eluted a red band which gave 1.14 g (2.67 mmol, 92% yield) of $(\mu-SCH=C(n-C_4H_9)S)Fe_2(CO)_6$ as a slightly air-sensitive red oil identified based on the following data:

IR ($CHCl_3$): 2957(s), 2925(s), 2870(m), 2860(m), 1462(m), 1419(m), 1376(m), 1190(broad), 1098(m), 924(w), 906(m), 710(m), 657(m), 611(s), 572(s), 547(s) cm^{-1} ;

terminal carbonyl region: 2075(vs), 2039(vs), 2000(vs), 1995(sh) cm^{-1} .

1H NMR ($CDCl_3$, 60MHz): δ 0.80 to 1.87 (m, 9H, butyl group) and 5.73 (s, 1H, vinyl).

^{13}C NMR ($CDCl_3$, 67.9MHz): δ_C 13.6 (q, $J = 125Hz$, CH_3), 21.9

(t, $J = 126\text{Hz}$, CH_2), 28.8 (t, $J = 125\text{Hz}$, CH_2), 33.5 (t, $J = 128\text{Hz}$, CH_2), 133.4 (d, $J = 183\text{Hz}$, $=\text{CH}$), 164.4 (s, $=\text{C}(\text{butyl})$) and 207.8 (s, CO).

Mass spectrum, m/z (relative intensity): 342 ($\text{M}^+ - 3\text{CO}$, 2), 314 ($\text{M}^+ - 4\text{CO}$, 8), 386 ($\text{M}^+ - 5\text{CO}$, 14), 258 ($\text{M}^+ - 6\text{CO}$, 37), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 18), 112 (Fe_2 , 10), 88 (FeS , 4), 56 (Fe , 18).

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2$: C, 33.83; H, 2.37%.

Found: C, 33.43; H, 2.32%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-heptyne and Trifluoroacetic Acid. (GBW-IV-10).

1-Lithio-1-heptyne, 7.0 mmol, was generated in 20 ml of THF from 0.93 ml (7.0 mmol) of 1-heptyne (Albany) and 7.0 mmol of lithium diisopropylamide. This reagent solution was cannulated into a 300 ml, three-necked flask containing 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 50 ml of THF cooled to -78°C , producing a green reaction mixture which was stirred for 30 min. Subsequently, 1.0 ml (13.46 mmol) of trifluoroacetic acid (Baker) was added causing an immediate color change to red. Stirring was continued at -78°C for 30 min then 30 min at room temperature prior to removal of solvent. The remaining brown tar was subjected to filtration chromatography (silicic acid/pentane); pentane eluted a red band which gave 0.99 g (2.25 mmol, 77% yield) of $(\mu\text{-SCH}=\text{C}(\text{n-C}_5\text{H}_{11})\text{S})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified based on the following data:

IR (CHCl_3): 2958(s), 2929(s), 2860(s), 1607(w) ($\text{C}=\text{C}$), 1468(m),

1460(sh), 1424(m), 1378(m), 1195(m), 1105(m), 716(m), 615(s), 560(vs) cm^{-1} ;

terminal carbonyl region: 2080(s), 2041(vs), 2007(vs) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 0.88 to 1.88 (m, 11H, pentyl group) and 5.77 (s, 1H, vinyl).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 13.8 (q, $J = 125\text{Hz}$, CH_3), 22.2 (t, $J = 124\text{Hz}$, CH_2), 26.4 (t, $J = 129\text{Hz}$, CH_2), 30.9 (t, $J = 125\text{Hz}$, CH_2), 33.7 (t, $J = 129\text{Hz}$, CH_2), 133.4 (d, $J = 183\text{Hz}$, $=\text{CH}$), 164.4 (s, $=\text{C}(\text{pentyl})$) and 207.8 (s, CO).

Mass spectrum, m/z (relative intensity): 412 ($\text{M}^+ - \text{CO}$, <1), 384 ($\text{M}^+ - 2\text{CO}$, <1), 356 ($\text{M}^+ - 3\text{CO}$, 1), 328 ($\text{M}^+ - 4\text{CO}$, 4), 300 ($\text{M}^+ - 5\text{CO}$, 8), 272 ($\text{M}^+ - 6\text{CO}$, 24), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 6), 112 (Fe_2 , 9), 88 (FeS , 2), 56 (Fe, 18).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_2$: C, 35.48; H, 2.75%.

Found: C, 35.68; H, 2.78%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-propyne and Trifluoroacetic Acid. (GBW-IV-4).

A dry, 100 ml, round-bottomed flask equipped with a magnetic stir-bar and a serum cap was flushed with nitrogen, charged with 20 ml of THF and cooled to -78°C . Propyne (Farchan), 1.50 ml (26.4 mmol), was condensed into the flask and 6.96 mmol of lithium diisopropylamide in THF was added. The solution was stirred for 30 min to allow formation of 1-lithiopropyne. This reagent solution was cannulated into a 300 ml, three-necked flask containing 1.0 g (2.91 mmol) of

$(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 50 ml of THF cooled to -78°C , producing a green reaction mixture which was stirred for 30 min. Subsequently, 0.6 ml (8.08 mmol) of trifluoroacetic acid (Baker) was added causing an immediate color change to red. Stirring was continued at -78°C for 1 h then at room temperature for 30 min prior to removal of solvent. The remaining brown solid was extracted with pentane until the extracts were colorless and the resulting red solution filtered. Removal of the solvent gave 0.85 g (2.21 mmol, 76% yield) of $(\mu\text{-SCH}=\text{C}(\text{Me})\text{S})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid, mp $61\text{-}62^\circ\text{C}$ after crystallization from pentane.

IR (CHCl_3): 2974(m), 2955(m), 2922(s), 2860(sh), 2849(m), 1613(w), 1424(s), 1373(m), 1160(m), 1083(s), 555(m) cm^{-1} ;

terminal carbonyl region: 2089(s), 2050(vs), 2010(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.61 (d, $J = 1.7\text{Hz}$, 3H, CH_3) and 5.77 (q, $J = 1.7\text{Hz}$, 1H, vinyl).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 19.6 (q, $J = 131\text{Hz}$, CH_3), 134.2 (d, $J = 183\text{Hz}$, $=\text{CH}$), 159.5 (s, $=\text{CMe}$) and 207.7 (s, CO).

Mass spectrum, m/z (relative intensity): 356 ($\text{M}^+ - \text{CO}$, 4), 328 ($\text{M}^+ - 2\text{CO}$, 5), 300 ($\text{M}^+ - 3\text{CO}$, 4), 272 ($\text{M}^+ - 4\text{CO}$, 5), 244 ($\text{M}^+ - 5\text{CO}$, 8), 216 ($\text{M}^+ - 6\text{CO}$, 21), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 25), 112 (Fe_2 , 19), 88 (FeS , 10), 56 (Fe, 35).

Anal. Calcd. for $\text{C}_9\text{H}_4\text{Fe}_2\text{O}_6\text{S}_2$: C, 28.15; H, 1.05%.

Found: C, 28.46; H, 1.16%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide and Trifluoroacetic Acid. (GBW-IV-14).

Ethynylmagnesium bromide, 28.2 mmol, was generated in 50 ml of THF from 17 ml (28.2 mmol) of a 1.66M THF ethylmagnesium bromide solution and acetylene (Airco) according to the procedure outlined on p. 75. The Grignard reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 15 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 1 h, 2.3 ml (31.0 mmol) of trifluoroacetic acid (Baker) was added causing an immediate color change to red. Stirring was continued for 10 min at -78°C then 1 h at room temperature prior to removal of solvent. The remaining red tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.57 g (1.54 mmol, 53% yield) of $(\mu\text{-SCH=CHS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid, mp $55\text{-}56^{\circ}\text{C}$ (lit.³⁵, mp $54\text{-}55^{\circ}\text{C}$) after crystallization from pentane.

IR (CHCl_3): $1564(\text{w}) (\text{C}=\text{C})$, $612(\text{m})$, $576(\text{s})$, $545(\text{s}) \text{ cm}^{-1}$;

terminal carbonyl region: $2087(\text{s})$, $2050(\text{vs})$, $2000(\text{vs}) \text{ cm}^{-1}$.

^1H NMR (CDCl_3 , 60MHz); δ 6.47 (s, vinyl).

^{13}C NMR (CD_3CN , 22.5MHz): δ_{C} 146.3 (dd, $J = 190\text{Hz}$, $^2J = 9\text{Hz}$, vinyl) and 209.2 (s, CO).

Anal. Calcd. for $\text{C}_8\text{H}_2\text{Fe}_2\text{O}_6\text{S}_2$: C, 25.98; H, 0.54%.

Found: C, 25.74; H, 0.62%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium (Trimethylsilyl)acetylide⁵⁰ and Trifluoroacetic Acid.

(GBW-V-1).

Lithium (trimethylsilyl)acetylide, 7.0 mmol, was generated in 30 ml of THF from 1.0 g (10.2 mmol) of trimethylsilylacetylene and 7.0 mmol of lithium diisopropylamide. This was cooled to -78°C and 1.0 g (2.91 mmol) of (μ -S₂)Fe₂(CO)₆ in 20 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 30 min at -78°C , 0.8 ml (10.8 mmol) of trifluoroacetic acid (Baker) was added causing a color change to red. Stirring was continued at -78°C for 30 min then 2.5 h at room temperature prior to removal of solvent. The remaining black solid was extracted with pentane/CH₂Cl₂ (9/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent from the red filtrate left a red oil which was applied to column chromatography (silicic acid/pentane). Pentane eluted two bands, the first yellow and the second red. The first band gave 0.37 g (0.84 mmol, 29% yield) of (μ -(Me₃Si)-CH=CS₂)Fe₂(CO)₆ as an air-stable, red solid, mp $47-49^{\circ}\text{C}$ after crystallization from ethanol.

IR (CHCl₃): 2958(m), 2800(w), 2870(sh), 1620(m), 1565(s), 1545(s), 1398(w), 1246(m), 1205(sh), 850(s), 610(m), 550(s) cm⁻¹;

terminal carbonyl region: 2083(vs), 2048(vs), 2005(s) cm⁻¹.

¹H NMR (CDCl₃, 90MHz): δ 0.12 (s, 9H, SiCH₃) and 4.86 (s, 1H, vinyl).

^{13}C NMR (CDCl_3 , 22.5MHz): δ_{C} -0.84 (q, $J = 119\text{Hz}$, SiCH_3), 115.4 (d, $J = 142\text{Hz}$, $=\text{CH}(\text{SiMe}_3)$), 157.9 (d, $J = 7\text{Hz}$, $=\text{CS}_2$) and 208.0 (s, CO).

Mass spectrum, m/z (relative intensity): 414 ($\text{M}^+ - \text{CO}$, 6), 386 ($\text{M}^+ - 2\text{CO}$, 8), 358 ($\text{M}^+ - 3\text{CO}$, 8), 330 ($\text{M}^+ - 4\text{CO}$, 9), 302 ($\text{M}^+ - 5\text{CO}$, 23), 274 ($\text{M}^+ - 6\text{CO}$, 100), 176 (Fe_2S_2 , 67), 144 (Fe_2S , 12), 112 (Fe_2 , 1), 56 (Fe, 2).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2\text{Si}$: C, 29.88; H, 2.28%.

Found: C, 30.00; H, 2.28%.

The second red band gave 0.58 g (1.32 mmol, 45% yield) of $(\mu\text{-SC}(\text{SiMe}_3)=\text{CHS})\text{Fe}_2(\text{CO})_6$ as an air-stable dark red solid, mp 69-70°C after crystallization from ethanol.

IR (CHCl_3): 2970(m), 2905(w), 1550(m), 1405(w), 1254(m), 1115(w), 900(s), 845(s), 830(sh), 620(m), 555(vs) cm^{-1} ;

terminal carbonyl region: 2000(vs), 2035(vs), 2077(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.04 (s, 9H, SiCH_3) and 6.43 (s, 1H, vinyl).

^{13}C NMR (CDCl_3 , 22.5MHz): δ_{C} -2.40 (q, $J = 111\text{Hz}$, SiCH_3), 150.8 (d, $J = 185\text{Hz}$, $=\text{CH}$), 159.7 (s, $=\text{CSiMe}_3$) and 207.9 (s, CO).

Mass spectrum, m/z (relative intensity): 414 ($\text{M}^+ - \text{CO}$, 4), 386 ($\text{M}^+ - 2\text{CO}$, 8), 358 ($\text{M}^+ - 3\text{CO}$, 13), 330 ($\text{M}^+ - 4\text{CO}$, 9), 302 ($\text{M}^+ - 5\text{CO}$, 23), 274 ($\text{M}^+ - 6\text{CO}$, 86), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 7), 112 (Fe_2 , 1), 56 (Fe, 7).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2\text{Si}$: C, 29.88; H, 2.28%.

Found: C, 29.84; H, 2.31%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Methyl 3-Li-thiopropiolate⁵¹ and Trifluoroacetic Acid. (GBW-III-67).

A dry, three-necked, 300 ml, round-bottomed flask equipped with a magnetic stir-bar and serum caps was flushed with nitrogen and charged with 30 ml of THF and 0.64 ml (4.5 mmol) of diisopropylamine (Eastman). This was cooled to 0°C and 2.0 ml (4.4 mmol) of a 2.2M n-BuLi solution (Alfa) was added. The reaction vessel was removed from the cold bath and stirred for 30 min to allow formation of the lithium diisopropylamide. Subsequently, the solution was cooled to -78°C and 0.40 ml (4.5 mmol) of methyl propiolate (Aldrich) was added dropwise by syringe and stirred for 30 min to form $\text{LiC}\equiv\text{CC}(\text{O})\text{OMe}$.⁵¹

This reagent solution was then cannulated into a 300 ml, three-necked flask containing 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 40 ml of THF cooled to -78°C, producing a brown reaction mixture which was stirred 30 min. Trifluoroacetic acid, 1.0 ml (13.46 mmol), was added and the reaction vessel was removed from the cold bath. Stirring was continued for 30 min prior to removal of the solvent. The remaining brown oil was taken up in CH_2Cl_2 and filtered through a pad of silicic acid. The red filtrate gave a dark red oil after removal of solvent which was applied to column chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.634 g (1.48 mmol, 51% yield) of $(\mu\text{-MeOC}(\text{O})\text{CH}=\text{CS}_2)\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 63-65°C after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 2960(m), 2850(w), 1700(s) (C=O), 1580(s) (C=C),

1433(m), 1300(s), 1270(sh), 1160(s), 1008(m), 957(m), 830(m), 609(m), 550(m) cm^{-1} ;

terminal carbonyl region: 2090(s), 2055(vs), 2015(vs) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 3.67 (s, 3H, CH_3) and 5.34 (s, 1H, vinyl).

^{13}C NMR (CD_2Cl_2 , 22.5MHz): δ_{C} 51.8 (q, $J = 147\text{Hz}$, CH_3), 108.4 (d, $J = 169\text{Hz}$, $=\text{CH}$), 165.3 (d, $^2J = 4\text{Hz}$, $=\text{CS}_2$), 166.4 (s, ester CO) and 207.9 (s, CO).

Mass spectrum, m/z (relative intensity): 400 ($\text{M}^+ - \text{CO}$, 5), 372 ($\text{M}^+ - 2\text{CO}$, 5), 344 ($\text{M}^+ - 3\text{CO}$, 5), 316 ($\text{M}^+ - 4\text{CO}$, 13), 288 ($\text{M}^+ - 5\text{CO}$, 7), 260 ($\text{M}^+ - 6\text{CO}$, 90), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 87), 112 (Fe_2 , 6), 88 (FeS , 6), 56 (Fe , 24).

Anal. Calcd. for $\text{C}_{10}\text{H}_4\text{Fe}_2\text{O}_8\text{S}_2$: C, 28.07; H, 0.94%.

Found: C, 27.63; H, 1.09%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Trimethylchlorosilane. (GBW-V-45).

A dry, three-necked, 300 ml, round-bottomed flask equipped with serum caps and a magnetic stir-bar was flushed with nitrogen and charged with 50 ml of THF and 0.77 ml (7.0 mmol) of phenylacetylene (Aldrich). This was cooled to -78°C and 3.15 ml (7.0 mmol) of a 2.2M hexane solution of n-butyllithium (Alfa) was added by syringe. The mixture was removed from the cold bath and stirred for 1 h to form the lithium phenylacetylide. The reagent solution was then cooled to -78°C , and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ dissolved in 15 ml of

THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 3.70 ml (29.2 mmol) of trimethylchlorosilane (Petrarch) was added by syringe. The solution was stirred for 15 min at -78°C and 19 h at room temperature during which time a color change of green-to-red occurred. The solvent was removed on a rotary evaporator leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after removal of solvent yielded an oily red solid. This material was crystallized from pentane/ethanol, mp $81-82^{\circ}\text{C}$, to yield 0.994 g (1.92 mmol, 66% yield) of $[\mu\text{-SC(Ph)=C(SiMe}_3\text{)S}]\text{Fe}_2(\text{CO})_6$ as an air stable, red solid identified on the basis of the following data:

IR (CHCl_3): 3054(m), 3000(m), 2950(s), 2892(m), 1596(m), 1570(m), 1480(m), 1441(m), 1404(m), 1263(s), 1245(s), 1070(m), 1026(m), 998(m), 923(s), 907(s), 840(s), 676(m), 603(s), 575(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2070(s), 2033(vs), 1998(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ -0.10 (s, 9H, SiCH_3), 7.04 and 7.29 (both m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -1.4 (q, $J = 120\text{Hz}$, SiCH_3), 126.6 (d, $J = 159\text{Hz}$, Ph), 128.5 (d, $J = 162\text{Hz}$, Ph), 129.3 (d, $J = 160\text{Hz}$, Ph), 136.8 (s, ipso Ph), 148.6 (s, $=\text{CSiMe}_3$), 167.2 (s, $=\text{CPh}$) and 208.3 (s, CO).

Anal. Calcd. for $C_{17}H_{14}Fe_2O_6S_2Si$: C, 39.40; H, 2.72%.

Found: C, 39.48; H, 2.84%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Trimethyltin Bromide. (GBW-V-38, VI-47).

Using the standard reaction vessel and procedure (p. 92), 3.19 mmol of $PhC\equiv CLi$ was generated in 40 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M hexane solution of n-butyllithium. This reagent solution was cooled to $-78^\circ C$ and 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at $-78^\circ C$, then 1.68 g (6.89 mmol) of trimethyltin bromide (Strem) was added by syringe. The solution was stirred for 30 min at $-78^\circ C$ and 6 h at room temperature during which time it became dark red. The solvent was removed leaving a red oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 1.61 g (2.64 mmol, 91% yield) of $[\mu-SC(SnMe_3)=C(Ph)S]Fe_2(CO)_6$ as an air-stable, red solid. After crystallization from pentane, mp $117-119^\circ C$ dec, it was identified based on the following data:

IR ($CHCl_3$): 3050(sh), 3023(m), 3000(m), 2980(m), 2912(m), 1597(m), 1567(w), 1484(m), 1442(m), 1229(w), 1189(m), 1070(m), 1027(m), 997(w), 918(m), 897(m), 795(m), 688(m), 615(s), 577(s), 550(s), 539(m) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2074(s), 2035(vs), 2000(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ -0.01 (s, $J(^{119}\text{Sn}-\text{H}) = 56.9\text{Hz}$, $J(^{117}\text{Sn}-\text{H})=54.7\text{Hz}$, 9Hz, SnCH_3), 7.08 and 7.28 (both m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -8.1 (q, $J = 131\text{Hz}$, SnCH_3), 126.3 (d, $J = 155\text{Hz}$, Ph), 128.5 (d, $J = 156\text{Hz}$, Ph), 129.3 (d, $J = 161\text{Hz}$, Ph), 137.0 (s, ipso Ph), 149.5 (s, $=\text{CSnMe}_3$), 156.1 (s, $=\text{CPh}$) and 208.2 (s, CO).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{Fe}_2\text{O}_6\text{S}_2\text{Sn}$: C, 33.54; H, 2.32%.

Found: C, 33.61; H, 2.38%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Triphenylgermanium Bromide. (GBW-VI-23).

Using the standard reaction vessel, 3.19 mmol of $\text{PhC}\equiv\text{CLi}$ was generated by the usual procedure (p. 92) and treated with 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ as before. To the resulting green solution at -78°C , was added 2.69 g (7.0 mmol) of triphenylgermanium bromide dissolved in 10 ml of THF. This solution was stirred at -78°C for 30 min and 16 h at room temperature during which time it became dark red. The solvent was removed leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.158 g (0.354 mmol, 12% yield) of $[\mu\text{-SCH}=\text{C}(\text{Ph})\text{S}]\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison to an authentic sample (p. 81). Pentane/ CH_2Cl_2 (4/1, v/v) eluted an orange band which yielded a red oily solid. The latter was again applied to filtration chromatography (silicic acid) which yielded 0.894 g (1.19 mmol, 41% yield) of $[\mu\text{-SC}(\text{Ph})=\text{C}(\text{GePh}_3)\text{S}]\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid. After crystallization from pentane/ CH_2Cl_2

mp 147-149°C dec , it was identified based on the following data:

IR (CHCl_3): 3070(sh), 3065(m), 3015(sh), 1570(broad), 1489(s), 1435(s), 1383(w), 1310(m), 1218(w), 1162(w), 1097(s), 1032(m), 1007(m), 910(m), 620(s), 560(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2082(s), 2051(vs), 2001(vs) cm^{-1} .

^1H NMR (d_6 -acetone, 90MHz): δ 6.90 (s, 5H, Ph) and 7.35 (s, 15H, GePh_3).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 126.5 (d, $J = 160\text{Hz}$, Ph), 127.8 (d, $J = 161\text{Hz}$, Ph), 128.3 (d, $J = 160\text{Hz}$, Ph), 129.2 (d, $J = 161\text{Hz}$, Ph), 129.3 (d, $J = 160\text{Hz}$, Ph), 134.0 (s, ipso Ph), 134.9 (d, $J = 160\text{Hz}$, Ph), 135.3 (s, ipso Ph), 144.5 (s, $=\text{CGePh}_3$), 169.1 (s, $=\text{CPh}$) and 208.1 (s, CO).

Anal. Calcd. for $\text{C}_{32}\text{H}_{20}\text{GeFe}_2\text{O}_6\text{S}_2$: C, 51.32; H, 2.69%.

Found: C, 51.30; H, 2.73%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Triphenyltin Chloride. (GBW-V-73).

Using the standard reaction vessel, 3.19 mmol of $\text{PhC}\equiv\text{CLi}$ was generated by the usual procedure (p. 92) and treated with 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ as before. To the resulting green solution at -78°C was added 3.47 g (9.0 mmol) of triphenyltin chloride (Alfa) dissolved in 10 ml of THF. This solution was stirred at -78°C for 30 min and 3 h at room temperature during which time it became dark red. The solvent was removed leaving

a red oil which was extracted with pentane until the extracts were colorless. The solvent was removed from the resulting red solution leaving a red solid which was applied to column chromatography (Florisil/pentane). Pentane eluted a red band which yielded 0.113 g (0.253 mmol, 9% yield) of $[\mu\text{-SCH}=\text{C}(\text{Ph})\text{S}]\text{-Fe}_2(\text{CO})_6$ as a red solid identified by comparison to an authentic sample (p. 81). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a second red band which yielded 1.98 g (2.49 mmol, 86% yield) of $[\mu\text{-S}(\text{Ph})\text{C}=\text{C}(\text{SnPh}_3)\text{S}]\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid. After crystallization from pentane/ CH_2Cl_2 , mp 127-128°C dec, it was identified based on the following data:

IR (CHCl_3): 3070(m), 3010(w), 1575(broad), 1487(s), 1448(m), 1433(s), 1378(w), 1337(m), 1305(m), 1263(w), 1162(w), 1080(s), 1029(m), 1004(s), 904(m), 618(s), 560(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2086(s), 2051(vs), 2005(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 6.92 (s, 5H, Ph) and 7.31 (s, 15H, SnPh_3).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 67.9MHz): δ_{C} 126.2, 128.1, 128.6, 128.7, 129.1, 129.3, 129.4 (all Ph), 136.6 (s, $J_{\text{C-Sn}} = 39\text{Hz}$, ipso, SnPh), 146.1 (s, $=\text{CSnPh}_3$), 170.7 (s, $=\text{CPh}$) and 208.0 (s, CO).

Anal. Calcd. for $\text{C}_{32}\text{H}_{20}\text{Fe}_2\text{S}_2\text{Sn}$: C, 48.35; H, 2.54%.

Found: C, 48.44; H, 2.56%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Triphenylead Bromide. (GBW-VI-53).

Using the standard reaction vessel, 3.19 mmol of $\text{PhC}\equiv\text{CLi}$

was generated by the usual procedure (p. 92) and treated with 2.91 mmol of $(\mu-S_2)Fe_2(CO)_6$ as before. To the resulting green solution at $-78^\circ C$ was added 4.67 g (9.0 mmol) of triphenyllead bromide dissolved in 10 ml of THF. This solution was stirred at $-78^\circ C$ for 30 min and 3 h at room temperature during which time it became red. The solvent was removed leaving a red oil which was dissolved in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The solvent was removed from the red filtrate leaving a red solid which was extracted with pentane until the extracts were colorless. The combined extracts were filtered and the solvent removed leaving a red solid which was applied to column chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.087 g (0.195 mmol, 7% yield) of $[\mu-SCH=C(Ph)S]Fe_2(CO)_6$ identified by comparison to an authentic sample (p. 81). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 1.79 g (2.03 mmol, 70% yield) of $[\mu-SC(Ph)=C(PbPh_3)S]Fe_2(CO)_6$ as an air-stable, red solid. After crystallization from pentane/ CH_2Cl_2 , mp $128-130^\circ C$ dec, it was identified based on the following data:

IR ($CHCl_3$): 3030(m), 1570(m), 1483(w), 1475(m), 1428(m), 1327(w), 1297(w), 1060(w), 1012(m), 993(m), 890(w), 689(s), 614(s), 573(s), 550(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2070(s), 2036(vs), 2000(vs) cm^{-1} .

1H NMR (acetone- d_6 , 90MHz): δ 7.39, 7.02 (both s, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 67.9MHz): δ_{C} 126.2, 128.1, 128.8 ($J_{\text{Pb-C}} = 23\text{Hz}$), 129.2, 129.6 ($J_{\text{Pb-C}} = 91\text{Hz}$), 135.8, 136.9 ($J_{\text{Pb-C}} = 73\text{Hz}$), 150.2 ($J_{\text{Pb-C}} = 545\text{Hz}$), (all Ph), 157.4 ($J_{\text{Pb-C}} = 63\text{Hz}$, $=\underline{\text{CPbPh}}_3$), 167.8 ($=\underline{\text{CPh}}$) and 208.1 (s, CO).

Anal. Calcd. for $\text{C}_{32}\text{H}_{20}\text{Fe}_2\text{O}_6\text{PbS}_2$: C, 43.50; H, 2.28%.

Found: C, 43.19; H, 2.25%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-hexyne and Trimethylchlorosilane. (GBW-V-49).

Using the standard reaction vessel and procedure (p. 92), 7.0 mmol of 1-lithio-1-hexyne was generated in 40 ml of THF from 0.88 ml (7.70 mmol) of 1-hexyne (Aldrich) and 3.14 ml (7.0 mmol) of a 2.2M hexane solution of n-butyllithium. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting a green reaction mixture. This was stirred for 30 min at -78°C , then 3.70 ml (29.2 mmol) of trimethylchlorosilane (Petrarch) was added by syringe. The solution was stirred for 30 min at -78°C and 14 h at room temperature during which time it became red. The solvent was removed leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 1.19 g (2.39 mmol, 82% yield) of $[\mu\text{-SC(n-Bu)=C(SiMe}_3)\text{S}]\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid. After crystallization from pentane/ethanol, mp $54\text{-}55^\circ\text{C}$, it was identified on the basis of the following data:

IR (CHCl_3): 2947(s), 2922(m), 2870(m), 2855(m), 1577(m) (C=C),

1455(m), 1404(m), 1377(m), 1245(s), 1120(m), 1098(w), 1053(m), 1027(w), 855(s), 846(s), 649(w), 607(s), 560(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2065(s), 2029(vs), 1996(vs), 1985(sh) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 0.14 (s, 9H, SiCH_3) and 0.80 to 2.24 (m, 9H, butyl).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -1.1 (q, $J = 120\text{Hz}$, SiCH_3), 13.7 (q, $J = 125\text{Hz}$, CH_3), 22.3 (t, $J = 125\text{Hz}$, CH_2), 29.2 (t, $J = 133\text{Hz}$, CH_2), 34.1 (t, $J = 130\text{Hz}$, CH_2), 143.7 (s, $=\text{CSiMe}_3$), 170.3 (s, $=\text{CCH}_2$) and 208.2 (s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Fe}_2\text{O}_6\text{S}_2\text{Si}$: C, 36.16; H, 3.64%.

Found: C, 36.23; H, 3.65%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-1-hexyne and Trimethyltin Chloride. (GBW-V-50).

Using the standard reaction vessel and procedure (p. 92), 4.40 mmol of $\text{LiC}\equiv\text{CC}_4\text{H}_9$ was generated in 40 ml of THF from 0.60 ml (5.23 mmol) of 1-hexyne (Aldrich) and 2.0 ml (4.40 mmol) of a 2.2M hexane solution of n-butyllithium. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 1.0 g (5.02 mmol) of Me_3SnCl in 10 ml of THF was cannulated into the reaction mixture. After stirring for 30 min at -78°C and 14 h at room temperature, the solution became dark red. The solvent was removed leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane

eluted a red band which after removal of solvent yielded 1.48 g (2.51 mmol, 86% yield) of $[\mu\text{-SC(n-Bu)=C(SnMe}_3\text{)S}]\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid. After recrystallization from pentane/ethanol, mp 48-49°C, it was identified based on the following data:

IR (CHCl_3): 2955(s), 2925(s), 2870(m), 2857(m), 1590(m), 1565(m), 1462(m), 1424(m), 1377(m), 1226(m), 1188(m), 1117(w), 1097(w), 1043(m), 1022(w), 923(w), 795(m), 610(s), 573(s), 550(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2069(s), 2031(vs), 1998(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.21 (s, $J(^{119}\text{Sn-H}) = 55.9\text{Hz}$, $J(^{117}\text{Sn-H}) = 54.6\text{Hz}$, SnCH_3) and 0.8 to 2.1 (m, butyl).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -8.3 (q, $J = 130\text{Hz}$, SnCH_3), 13.8 (q, $J = 124\text{Hz}$, CH_3), 22.2 (t, $J = 126\text{Hz}$, CH_2), 29.6 (t, $J = 130\text{Hz}$, CH_2), 34.9 (t, $J = 130\text{Hz}$, CH_2), 143.8 (s, $=\text{CSnMe}_3$), 169.2 (s, $=\text{CCH}_2$) and 208.3 (s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Fe}_2\text{O}_6\text{S}_2\text{Sn}$: C, 30.60; H, 3.08%.

Found: C, 30.71; H, 3.13%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), 1-Lithio-propyne and Trimethyltin Chloride. (GBW-V-19).

Following the procedure on (p. 86), 5.5 mmol of 1-lithio-propyne was generated in a 300 ml, three-necked flask using 30 ml of THF, 1.5 ml (26.4 mmol) of propyne (Farchan) and 2.5 ml (5.50 mmol) of a 2.2M n-BuLi solution (Alfa). Into this solution, at -78°C, 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$

in 20 ml of THF was cannulated producing a green reaction mixture. After stirring for 30 min, 1.10 g (5.52 mmol) of trimethyltin chloride in 10 ml of THF was cannulated into the solution. Stirring was continued at -78°C for 30 min then for 1 h at room temperature. The solvent was removed leaving a brown oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 1.19 g (2.18 mmol, 75% yield) of $[\mu\text{-SC(Me)=C(SnMe}_3\text{)S}]\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp $74\text{--}75^{\circ}\text{C}$ after crystallization from pentane/ethanol.

IR (CHCl_3): 2980(m), 2907(m), 1605(m), 1570(m), 1428(m), 1370(m), 1225(w), 1188(m), 1090(m), 991(w), 922(w), 795(m), 700(w), 608(s), 570(s), 550(s) cm^{-1} ;

terminal carbonyl region: 2068(s), 2030(vs), 1998(vs) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 0.22 (s, 9H, $J(^{119}\text{Sn-H}) = 57.0\text{Hz}$, $J(^{117}\text{Sn-H}) = 54.0\text{Hz}$, SnCH_3) and 1.72 (s, 3H, CH_3).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -8.5 (q, $J = 130\text{Hz}$, SnCH_3), 21.1 (q, $J = 129\text{Hz}$, CH_3), 143.7 (s, $=\text{CSnMe}_3$), 163.8 (s, $=\text{CMe}$) and 208.2 (s, CO).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_2\text{Sn}$: C, 26.36; H, 2.21%.

Found: C, 26.54; H, 2.29%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Methyl 3-Lithiopropiolate and Trimethylchlorosilane. (GBW-V-54).

Using the procedure outlined on (p. 91), 4.4 mmol of $\text{LiC}\equiv\text{CC(O)OMe}$ was generated at -78°C from 4.4 mmol of lithium

diisopropylamide and 0.64 ml (4.5 mmol) of methyl propiolate (Aldrich). Dissolved in 20 ml of THF, 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ was cannulated into the lithium reagent solution resulting in a brown reaction mixture. After stirring for 30 min, 3.70 ml (29.2 mmol) of Me_3SiCl (Petrarch) was added by syringe. The solution was stirred at $-78^\circ C$ for 15 min then at room temperature for 14 h during which time it became dark red. Removal of the solvent left a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 1.0 g (2.0 mmol, 69% yield) of $[\mu-MeOC(O)C(SiMe_3)=CS_2]Fe_2(CO)_6$ as an air-stable, red solid, mp $46-47^\circ C$ after crystallization from pentane.

IR ($CHCl_3$): 3000(w), 2948(m), 2893(w), 1700(s) (C=O), 1545(sh), 1525(s) (C=C), 1430(m), 1227(s, broad), 1047(m), 977(w), 918(w), 839(s), 683(w), 608(s), 560(s) cm^{-1} ;

terminal carbonyl region: 2076(s), 2039(vs), 2002(vs) cm^{-1} .

1H NMR ($CDCl_3$, 90MHz): δ 0.18 (s, 9H, $SiCH_3$) and 3.67 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 67.9MHz): δ_C -0.64 (q, $J = 120Hz$, $SiCH_3$), 51.4 (q, $J = 147Hz$, CH_3), 121.8 (s, $=CSiMe_3$), 165.4 (s, $=CS_2$), 167.1 (s, ester CO) and 207.4 (s, CO).

Anal. Calcd. for $C_{13}H_{12}Fe_2O_8S_2Si$: C, 31.22; H, 2.42%.

Found: C, 31.37; H, 2.47%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Methyl 3-Li-thiopropiolate and Trimethyltin Chloride. (GBW-V-60).

Using the procedure outlined on (p. 91), 4.5 mmol of $\text{LiC}\equiv\text{CC}(\text{O})\text{OMe}$ was generated at -78°C from 4.5 mmol of lithium diisopropylamide and 4.5 mmol of methyl propiolate (Aldrich). Dissolved in 10 ml of THF, 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ was cannulated into the lithium reagent solution resulting in a brown reaction mixture. After stirring for 30 min, 1.0 g (5.02 mmol) of trimethyltin chloride in 10 ml of THF was cannulated into the reaction mixture. Stirring was continued for 45 min at -78°C then the solvent was removed on a rotary evaporator. The remaining brown oil was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted an orange band which yielded a red oily solid. After crystallization from pentane, 0.68 g (1.15 mmol, 40%) of $[\mu\text{-MeOC}(\text{O})\text{C}(\text{SnMe}_3)=\text{CS}_2]\text{Fe}_2(\text{CO})_6$ was obtained as an air-stable, red solid, mp $71\text{-}72^\circ\text{C}$.

IR (CHCl_3): 2975(m), 2938(m), 2904(m), 2849(w), 1685(s) ($\text{C}=\text{O}$), 1525(s) ($\text{C}=\text{C}$), 1425(m), 1295(m), 1222(s), 1180(s), 1023(s), 960(m), 892(w), 825(m), 604(s), 560(s), 550(s) cm^{-1} ;

terminal carbonyl region: 2079(s), 2043(vs), 2006(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.29 (s, $J(^{119}\text{Sn-H}) = 57.6\text{Hz}$, $J(^{117}\text{Sn-H}) = 54.7\text{Hz}$, 9H, SnCH_3), 3.65 (s, 3H, CH_3).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} -6.9 (q, $J = 130\text{Hz}$, SnCH_3), 51.4 (q, $J = 147\text{Hz}$, CH_3), 121.7 (s, $=\text{CSnMe}_3$), 165.6 (s, $=\text{CS}_2$), 167.7 (s, ester CO) and 207.4 (s, CO).

Anal. Calcd. for $C_{13}H_{12}Fe_2O_8S_2Si$: C, 26.43; H, 2.05%.

Found: C, 26.69; H, 2.08%.

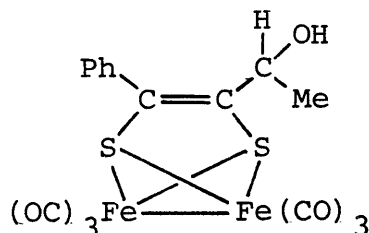
Reaction Between (μ -Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide⁴⁹ and Trimethylchlorosilane. (GBW-IV-35).

Ethynylmagnesium bromide (18.0 mmol) was made according to the procedure outlined on (p. 75), using 50 ml of THF and 10 ml (18.0 mmol) of a 1.80M THF solution of EtMgBr. The Grignard reagent solution was cooled to -78°C , and 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. After stirring for 1.5 h at -78°C , 2.30 ml (18.4 mmol) of Me_3SiCl (Petrarch) was added. Stirring was continued for 30 min at -78°C and 1.5 h at room temperature during which time the solution became red. The solvent was removed leaving a black solid which was applied to filtration chromatography (silicic acid /pentane). Pentane eluted a red band which yielded 0.517 g (1.17 mmol, 40% yield) of $[\mu-SCH=C(SiMe_3)S]Fe_2(CO)_6$ as an air-stable, red solid. After crystallization from ethanol, mp $69-70^\circ\text{C}$, it was identified by comparison of its 1H NMR spectra to that of an authentic sample.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Acetaldehyde. (GBW-VI-24).

Following the standard procedure (p. 92), 3.19 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This reagent

solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{-Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 4 ml (71.1 mmol) of acetaldehyde (Baker) was added by syringe. The mixture was stirred for 30 min at -78°C and 2 h at room temperature resulting in a red solution. Trifluoroacetic acid, 0.4 ml (5.38 mmol), was added and the solution stirred another 30 min prior to removal of the solvent. The remaining brown oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.52 g (1.16 mmol, 40% yield) of $(\mu\text{-SCH=C(Ph)S})\text{Fe}_2(\text{CO})_6$ identified by comparison to an authentic sample. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a minor black band (not collected) and pentane/ Et_2O (4/1, v/v) moved a red band which gave 0.49 g of a red tar. This tar was applied to column chromatography (silicic acid/ CH_2Cl_2), CH_2Cl_2 eluting a red band which gave 0.44 g (0.89 mmol, 31% yield) of an air-stable red solid, mp $87\text{-}89^{\circ}\text{C}$ after crystallization from CH_2Cl_2 /pentane, identified as:



IR (CHCl_3): 3608(m) (O-H), 3450 (broad) (O-H), 2988(m), 2940(w), 1615(w), 1598(w), 1578(w), 1492(m), 1449(m), 1380(m), 1330(m), 1255(m), 1140(m), 1051(s), 1006(w), 971(m), 927(w), 905(m),

856(m), 620(s), 560(s) cm^{-1} ;

terminal carbonyl region: 2088(s), 2062(vs), 2004(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 1.34 (d, $J = 6.3\text{Hz}$, 3H, CH_3), 1.55 (d, $J = 5.9\text{Hz}$, 1H, OH), 4.19 (quintet, $J = 6.3\text{Hz}$, 1H, CH), 7.34 (m, 3H, Ph) and 7.07 (m, 2H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 20.6 (q, $J = 128\text{Hz}$, CH_3), 64.9 (d, $J = 150\text{Hz}$, CH), 126.3 (d, $J = 155\text{Hz}$, Ph), 128.7 (d, $J = 166\text{Hz}$, Ph), 129.2 (d, $J = 166\text{Hz}$, Ph), 134.4 (s, ipso Ph), 151.6 (s, vinyl), 155.8 (s, vinyl) and 207.6 (s, CO).

Mass spectrum, m/z (relative intensity): 434 ($\text{M}^+ - 2\text{CO}$, 3), 406 ($\text{M}^+ - 3\text{CO}$, 7), 378 ($\text{M}^+ - 4\text{CO}$, 5), 350 ($\text{M}^+ - 5\text{CO}$, 15), 322 ($\text{M}^+ - 6\text{CO}$, 22), 304 ($\text{M}^+ - 6\text{CO} - \text{H}_2\text{O}$, 60), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 12), 88 (FeS , 6), 77 (Ph, 34), 56 (Fe, 10).

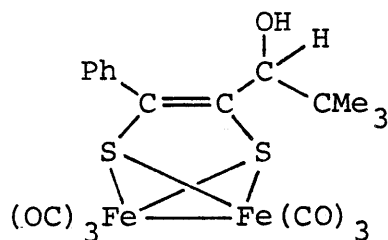
Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{Fe}_2\text{O}_7\text{S}_2$: C, 39.21; H, 2.06%.

Found: C, 39.44; H, 2.07%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Pivalaldehyde. (GBW-VI-26).

Following the standard procedure (p. 92), 3.19 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of ($\mu\text{-S}_2$)- $\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 1.09 ml (10.0 mmol) of pivalaldehyde (Aldrich) was added

by syringe. The mixture was stirred for 30 min at -78°C and 1.5 h at room temperature. Trifluoroacetic acid, 0.3 ml (4.04 mmol), was added and the solution stirred another 30 min prior to removal of the solvent. The remaining brown oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band (trace amount of a red, oily solid not identified), pentane/ CH_2Cl_2 (4/1, v/v) moved a minor black band (not identified) and pentane/ Et_2O (4/1, v/v) eluted a red band giving 1.28 g of a red tar. This tar was subjected to column chromatograph (silicic acid/ CH_2Cl_2), CH_2Cl_2 eluting a red band which gave 1.18 g (2.21 mmol, 76% yield) of an air-stable red solid, mp $92-94^{\circ}\text{C}$ after crystallization from CH_2Cl_2 /pentane, identified as:



IR (CHCl_3): 3597(m) (O-H), 3470(broad) (O-H), 2970(s), 2920(sh), 2884(m), 1615(w), 1596(w), 1578(w), 1480(m), 1467(m), 1448(m), 1402(m), 1372(s), 1180(m), 1098(m), 1078(m), 1040(m), 1011(s), 942(w), 927(w), 910(w), 870(m), 618(s), 560(s) cm^{-1} ;

terminal carbonyl region: 2089(s), 2051(vs), 2002(vs) cm^{-1} .

^1H NMR (acetone- d_6 , 90MHz): δ 3.74 and 4.50 (both d, $J = 5.9\text{Hz}$, 2H, OH and CH), 0.80 (s, 12H, $\text{C}(\text{CH}_3)_2$), 7.10 (m, 2H, Ph) and 7.32 (m, 3H, Ph).

^{13}C NMR (CDCl_3 , 67.9Hz): δ_{C} 26.6 (q, $J = 128\text{Hz}$, CH_3), 36.4 (s, CMe_3), 77.0 (d, $J = 148\text{Hz}$, CH), 126.5 (d, $J = 169\text{Hz}$, Ph), 129.0 (d, $J = 161\text{Hz}$, Ph), 135.5 (s, ipso Ph), 153.7 (s, vinyl), 153.9 (s, vinyl), 207.6 and 207.9 (both s, CO).

Mass spectrum, m/z (relative intensity): 476 ($\text{M}^+ - 2\text{CO}$, 9), 448 ($\text{M}^+ - 3\text{CO}$, 15), 420 ($\text{M}^+ - 4\text{CO}$, 7), 392 ($\text{M}^+ - 5\text{CO}$, 6), 364 ($\text{M}^+ - 6\text{CO}$, 100), 346 ($\text{M}^+ - 6\text{CO} - \text{H}_2\text{O}$, 74), 176 (Fe_2S_2 , 76), 112 (Fe_2 , 5), 88 (FeS , 16), 77 (Ph, 100), 56 (Fe, 80).

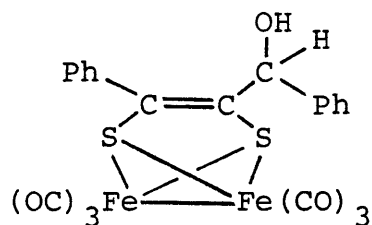
Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{Fe}_2\text{O}_7\text{S}_2$: C, 42.88; H, 3.03%.

Found: C, 42.69; H, 3.09%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Benzaldehyde. (GBW-VI-8).

Following the standard procedure (p. 92), 3.19 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.35 ml (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n -butyllithium solution. This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of (μ - S_2)- $\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at -78°C , then 0.92 ml (9.0 mmol) of benzaldehyde (Aldrich) was added by syringe. The mixture was stirred for 1 h at -78°C and 2.5 h at room temperature. The reaction mixture was acidified with 10 ml of a 2.4M HCl solution. After stirring 15 min the solvent was removed on a rotary evaporator leaving a black tar which was taken up in Et_2O and washed with water. The organic layer was dried with MgSO_4 and filtered. Removal of the solvent

left a black tar which was applied to filtration chromatography (silicic acid/pentane), pentane/ CH_2Cl_2 (4/1, v/v) eluted a minor red band (not identified) and pentane/ Et_2O (4/1, v/v) moved an orange band giving 0.84 g of a red tar. This tar was applied to column chromatography (silicic acid/ CH_2Cl_2); CH_2Cl_2 eluting a red band which yielded 0.76 g (1.38 mmol, 47% yield) of an air-stable, red, glassy solid identified as:



IR (CHCl_3): 3593(m) (O-H), 3400(broad) (O-H), 3069(w), 3012(w), 1596(w), 1577(w), 1492(m), 1454(sh), 1447(m), 1371(m), 1176(w), 1096(sh), 1078(m), 1017(m), 920(w), 891(w), 614(s), 560(s) cm^{-1} ;

terminal carbonyl region: 2087(s), 2051(vs), 2014(vs) cm^{-1} .

^1H NMR (CD_3CN , 270MHz): δ 3.86 and 5.05 (both d, 2H, $J = 5.2\text{Hz}$, OH and CH), 7.22 and 7.36 (both m, 10H, Ph).

^{13}C NMR (CDCl_3 , 67.9Hz): δ_{C} 70.3 (d, $J = 146\text{Hz}$, CH), 125.5 (d, $J = 160\text{Hz}$, Ph), 126.4 (d, $J = 160\text{Hz}$, Ph), 128.1 (d, $J = 160\text{Hz}$, Ph), 128.6 (d, $J = 160\text{Hz}$, Ph), 128.8 (d, $J = 162\text{Hz}$, Ph), 129.4 (d, $J = 162\text{Hz}$, Ph), 134.4 (s, ipso Ph), 138.9 (s, ipso Ph), 153.1, 154.0 (both s, vinyl), 207.4 and 207.6 (both s, CO).

Mass spectrum, m/z (relative intensity): 524 ($\text{M}^+ - \text{CO}$, 4), 496 ($\text{M}^+ - 2\text{CO}$, 19), 468 ($\text{M}^+ - 3\text{CO}$, 28), 440 ($\text{M}^+ - 4\text{CO}$, 15), 412 ($\text{M}^+ - 5\text{CO}$,

11), 384 ($M^+ - 6CO$, 100), 176 (Fe_2S_2 , 24), 144 (Fe_2S , 4), 88 (FeS , 11), 77 (Ph, 46), 56 (Fe, 10).

Anal. Calcd. for $C_{21}H_{12}Fe_2O_7S_2$: C, 45.68; H, 2.19%.

Found: C, 45.44; H, 2.23%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Methylmercuric Chloride. (GBW-VI-2, XI-16).

Following the standard procedure (p. 92), 3.19 mmol of lithium phenylacetylide was generated in 40 ml of THF from 0.35 ml phenylacetylene (Aldrich) and 1.45 ml (3.19 mmol) of a 2.2M n-butyllithium solution. This solution was cooled to $-78^\circ C$ and 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it resulting in a green reaction mixture. This was stirred for 30 min at $-78^\circ C$, then 0.83 g (3.30 mmol) of methylmercuric chloride (Organometallics) in 10 ml of THF was cannulated in causing a color change to red. The mixture was stirred for 30 min at $-78^\circ C$ and 30 min at room temperature prior to removal of the solvent. The remaining red oil was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red solid which was applied to filtration chromatography (silicic acid /pentane). Pentane eluted two red bands which gave respectively, 0.23 g (0.51 mmol, 18% yield) of $(\mu-SCH=C(Ph)S)Fe_2(CO)_6$ identified by comparison to an authentic sample and 0.30 g (0.45 mmol, 16% yield) of $[\mu-SC(HgMe)=C(Ph)S]Fe_2(CO)_6$ as an air-stable red solid, mp $123-130^\circ C$ dec after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 2915(m), 1594(m), 1550(m, broad), 1487(m), 1447(m), 1078(m), 907(m), 617(s), 555(s) cm^{-1} ;

terminal carbonyl region: 2079(s), 2045(vs), 2004(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 270MHz): δ 0.53 (s, $J_{\text{H}_{\text{g-H}}}$ = 135.2Hz, 3H, CH_3) and 7.30 (m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 11.2 (q, J = 133Hz, CH_3), 125.2 (d, J = 158Hz, Ph), 128.6 (d, J = 162Hz, Ph), 129.4 (d, J = 162Hz, Ph), 136.4 (s, ipso Ph), 167.3 (s, vinyl), 189.1 (s, vinyl and 208.2 (s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2\text{Hg}$: C, 27.27; H, 1.22%.

Found: C, 27.35; H, 1.46%.

Pentane/ CH_2Cl_2 (4/1, v/v) eluted a third red band which yielded 1.0 g (1.52 mmol, 52% yield) of $(\mu\text{-MeHgS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ as a dark red air-stable solid, mp 125-130°C dec after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 2925(w), 2174(w) ($\text{C}\equiv\text{C}$), 1597(m), 1489(m), 1443(m), 1267(m), 912(w), 861(w), 614(s), 560(s) cm^{-1} ;

terminal carbonyl region: 2080(s), 2047(vs), 2004(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 270MHz): δ 0.91 (s, $J_{\text{H}_{\text{g-H}}}$ = 165.6Hz, 3H, CH_3) and 7.38 (m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 17.5 (q, J = 138Hz, CH_3), 84.9 (s, alkynyl), 85.1 (s, alkynyl), 122.0 (s, ipso Ph), 128.4 (d, J = 162Hz, Ph), 129.1 (d, J = 162Hz, Ph), 132.2 (d, J = 164Hz, Ph) and 208.8 (s, CO).

Anal. Calcd. for $C_{15}H_8Fe_2O_6S_2Hg$: C, 27.27; H, 1.22%.

Found: C, 27.32; H, 1.29%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Methylmercuric Chloride at $-78^\circ C$. (GBW-VI-29).

Following the procedure outlined on (p. 92), 3.19 mmol of lithium phenylacetylide was reacted with 1.0 g (2.91 mmol) of $(\mu-S_2)Fe_2(CO)_6$ at $-78^\circ C$ resulting in a green reaction mixture. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 ml of THF, was cannulated into the reaction mixture producing a red solution which was stirred for 4.5 h at $-78^\circ C$. It was then taken from the cold bath and the solvent removed on a rotary evaporator. The remaining red oil was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red solid which was extracted with two 30 ml portions of pentane, leaving much of the solid but giving a red filtrate. This pentane solution was subjected to filtration chromatography (silicic acid/pentane) giving two red bands which yielded respectively, 0.044 g (0.099 mmol, 3% yield) of $[\mu-SCH=C(Ph)S]Fe_2(CO)_6$ and 0.11 g (0.16 mmol, 6% yield) of $(\mu-SC(HgMe)=C(Ph)S)Fe_2(CO)_6$ both identified by comparison of their 1H NMR spectra to those of the authentic samples. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a third red band which was combined with the extracted red solid to give 1.52 g (2.30 mmol, 79% yield) of $(\mu-MeHgS)(\mu-PhC\equiv CS)Fe_2(CO)_6$ identified by comparison of its 1H NMR spectrum to that of an authentic sample.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Methylmercuric Chloride, 1 h at -78°C and 4.5 h at Room Temperature. (GBW-VI-33).

Following the procedure outlined on (p. 92), 3.19 mmol of lithium phenylacetylide was reacted with 1.0 g (2.91 mmol) of (μ -S₂)Fe₂(CO)₆ at -78°C resulting in a green reaction mixture. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 ml of THF, was cannulated into the reaction mixture producing a red solution which was stirred for 1 h at -78°C . It then was removed from the cold bath and stirred at room temperature for 4.5 h prior to removal of solvent. The remaining red tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.32 g (0.71 mmol, 25% yield) of (μ -SCH=C(Ph)S)Fe₂(CO)₆ and pentane/CH₂Cl₂ (4/1, v/v) eluted a red band which gave 1.02 g (1.54 mmol, 53% yield) of [μ -SC(HgMe)=C(Ph)]Fe₂(CO)₆ both identified by comparison of their ¹H NMR spectra to those of an authentic sample.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Methylmercuric Chloride at Room Temperature. (GBW-VI-27).

Following the procedure outlined on (p. 92), 3.19 mmol of lithium phenylacetylide was added to 1.0 g (2.91 mmol) of (μ -S₂)Fe₂(CO)₆ at -78°C resulting in a green reaction mixture. The solution was removed from the cold bath and stirred for 35 min at which point it looked brown. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 ml of THF, was cannulated into the reaction mixture producing a red solution which was stirred for

5 h. The solvent was removed on a rotary evaporator leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band which gave 0.117 g (0.262 mmol, 9% yield) of $(\mu\text{-CH=C(Ph)})\text{Fe}_2(\text{CO})_6$; pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 1.28 g (1.94 mmol, 67% yield) of $(\mu\text{-SC(HgMe)=C(Ph)S})\text{Fe}_2(\text{CO})_6$. Both products were identified by comparison of their ^1H NMR spectra to those of the authentic samples.

Isomerization of $(\mu\text{-MeHgS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ in the Presence of Lithium Chloride. (GBW-VI-44).

A dry, 100 ml, round-bottomed flask equipped with a stir-bar and a serum cap was charged with 0.83 g (1.26 mmol) of $(\mu\text{-MeHgS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ and 0.05 g (1.26 mmol) of anhydrous lithium chloride in a glove box. After removal from the glove box, 40 ml of THF was added and the solution stirred for 3 h. The solvent was removed on a rotary evaporator leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band which yielded 0.096 g (0.22 mmol, 17% yield) of $(\mu\text{-CH=C(Ph)S})\text{Fe}_2(\text{CO})_6$; further elution with pentane/ CH_2Cl_2 (9/1, v/v) moved a red band which gave 0.65 g (0.98 mmol, 78% yield) of $[\mu\text{-SC(HgMe)=C(Ph)S}]\text{Fe}_2(\text{CO})_6$, both were identified by comparison of their ^1H NMR spectra to those of the authentic samples.

Reaction between $[\mu\text{-SC(SnPh}_3\text{)=C(Ph)S}]\text{Fe}_2(\text{CO})_6$, Phenyllithium and Iodomethane. (GBW-VI-4, X-61).

A dry, 300 ml, round-bottomed flask equipped with a

magnetic stir-bar and a serum cap was charged with 0.38 g (0.48 mmol) of $[\mu\text{-SC}(\text{SnPh}_3)=\text{C}(\text{Ph})\text{S}]\text{Fe}_2(\text{CO})_6$ and flushed with nitrogen. Diethyl ether (30 ml) was added and the red solution cooled to -78°C . By syringe, 0.84 ml (0.72 mmol) of a 0.86M phenyllithium solution was added and the reaction mixture stirred for 1 h. The solution became red-brown and a white precipitate (Ph_4Sn) was observed. Subsequently, 1 ml of iodomethane was added and the solution was stirred for 0.5 h at -78°C and 2 h at room temperature. The reaction mixture was filtered and the white solid obtained washed with water and Et_2O . After drying, this solid was identified as Ph_4Sn (mp $229\text{-}231^\circ\text{C}$, lit.⁵² $228\text{-}230^\circ\text{C}$), 0.103 g (0.24 mmol, 50% yield). The solvent was removed from the red filtrate leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.14 g (0.30 mmol, 63% yield) of $(\mu\text{-MeS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$, identified by comparison of its IR, ^1H NMR and ^{13}C NMR spectra to those of an authentic sample and was found to be a 1.4/1 (CH_3 a/ CH_3 e) mixture of both isomers.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Triphenyltin Chloride in Diethyl Ether.

(GBW-XI-27).

Following the standard procedure (p. 92), 3.19 mmol of lithium phenylacetylide was generated in 30 ml of Et_2O . This reagent solution was cooled to -78°C and 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 20 ml of Et_2O was cannulated into it resulting

in a brown solution. This was stirred for 30 min at -78°C , then 1.16 g (3.0 mmol) of Ph_3SnCl (Alfa) was added as a solid against a counterflow of nitrogen. The solution was stirred for 30 min at -78°C during which time the solution became red and a white precipitate (LiCl) formed. It was then removed from the cold bath and stirred another 45 min. The solution then was filtered and the diethyl ether removed leaving a red oil. This oil was taken up in pentane and filtered. Removal of the solvent left a red tar which was dried under vacuum. This was dissolved in pentane and concentrated to about 5 ml. A red solid, 0.61 g (0.77 mmol, 26% yield), was deposited overnight at room temperature. The material, mp $105\text{--}107^{\circ}\text{C}$ dec, was identified as $(\mu\text{-Ph}_3\text{SnS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$.

IR (CHCl_3): 3078(m), 3002(w), 2172(w) ($\text{C}\equiv\text{C}$), 1597(w), 1574(w), 1482(m), 1431(m), 1334(w), 1302(w), 1074(m), 1023(w), 997(m), 856(w), 694(s), 615(s), 560(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2079(s), 2043(vs), 2005(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 7.25 to 7.8 (complex m, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 86.6, 86.9 (alkyne), 122.8 (ipso $\equiv\text{CPh}$), 129 to 139.6 (Ph) and 208.7 (s, CO).

Anal. Calcd. for $\text{C}_{32}\text{H}_{20}\text{Fe}_2\text{O}_6\text{SnS}_2$: C, 48.34; H, 2.54%.

Found: C, 48.16; H, 2.60%.

Reaction Between (μ -Dithio)bis(tricarbonyliron), Lithium Phenylacetylide and Triphenyllead Chloride in Diethyl Ether.

(GBW-XI-26, XI-29).

Using the standard reaction procedure (p. 92), 1.50 mmol of lithium phenylacetylide was generated in 30 ml of Et₂O and treated with 0.5 g (1.46 mmol) of (μ -S₂)Fe₂(CO)₆ as before. The resulting brown solution was stirred for 30 min at -78°C then, against a counterflow of nitrogen, 0.78 g (1.50 mmol) of Ph₃PbBr was added as a solid. The solution was stirred for 30 min at -78°C during which time it became red and a white precipitate formed (LiBr). It then was removed from the cold bath and stirred another 3 h at room temperature. After filtering the solution, the diethyl ether was removed leaving a red tar. This tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH₂Cl₂ (9/1, v/v) eluted a red band which gave 0.91 g (1.03 mmol, 71% yield) of (μ -Ph₃PbS)-(μ -PhC \equiv CS)Fe₂(CO)₆ as a glassy, red solid.

IR (CHCl₃): 3078(m), 2175(w) (C \equiv C), 1600(w), 1573(m), 1490(m), 1477(m), 1432(s), 1332(w), 1301(w), 1061(m), 1027(m), 998(s), 855(w), 691(s), 615(s), 560(s) cm⁻¹;

terminal carbonyl region (CHCl₃): 2079(s), 2044(vs), 2007(vs) cm⁻¹.

¹H NMR (CD₂Cl₂, 90MHz): δ 7.1 to 7.8 (complex m, Ph).

¹³C {¹H} NMR (CD₂Cl₂, 67.9MHz): δ _C 86.1, 87.0 (alkyne) 122.7 (ipso \equiv CPh), 129 to 132.5 (Ph), 155.5 (J_{C-Pb} = 438Hz, ipso PbPh) and

209.1 (CO).

Anal. Calcd. for $C_{32}H_{20}Fe_2O_6PbS$: C, 43.50; H, 2.28%.

Found: C, 43.73; H, 2.44%.

Addition of $(\mu-Ph_3PbS)(\mu-PhC\equiv CS)Fe_2(CO)_6$ to a THF Solution of Lithium Bromide. (GBW-XI-32).

A 100 ml, round-bottomed flask was charged with 0.05 g (0.57 mmol) of anhydrous lithium bromide and 10 ml of THF. After cooling this solution to $-78^\circ C$, 0.50 g (0.57 mmol) of $(\mu-Ph_3PbS)(\mu-PhC\equiv CS)Fe_2(CO)_6$ in 10 ml of THF was cannulated into it. The mixture became brown and was stirred at $-78^\circ C$ for 2 h. It was then removed from the cold bath and stirred another 3 h prior to removal of the solvent. The black tar remaining was extracted with pentane yielding a red solution. This was subjected to filtration chromatography (silicic acid /pentane). Pentane eluted a red band which gave 0.065 g (0.146 mmol, 26% yield) of $(\mu-SCH=CPhS)Fe_2(CO)_6$ as a red solid identified by comparison of its 1H NMR spectrum to that of an authentic sample.

Addition of $(\mu-Ph_3PbS)(\mu-PhC\equiv CS)Fe_2(CO)_6$ and Triphenyllead Bromide to a THF Solution of Lithium Bromide. (GBW-XI-33).

Using the same procedure as before, a mixture of 0.40 g (0.45 mmol) of $(\mu-Ph_3PbS)(\mu-PhC\equiv CS)Fe_2(CO)_6$, 0.47 g (0.90 mmol) of Ph_3PbBr and 20 ml of THF was cannulated into a $-78^\circ C$, 10 ml THF solution of 0.04 g (0.45 mmol) of anhydrous lithium bromide. The solution was stirred for 30 min at $-78^\circ C$ and 4 h at room temperature. The solvent was removed and the remaining black

tar extracted with pentane. The red pentane solution was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.055 g (0.12 mmol, 27% yield) of $(\mu\text{-SCH=CPHS})\text{Fe}_2(\text{CO})_6$ as a red solid, identified by comparison of its ^1H NMR spectrum to that of an authentic sample.

Addition of $(\mu\text{-Ph}_3\text{SnS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ to a THF Solution of Lithium Chloride. (GBW-XI-40).

A 100 ml, round-bottomed flask was charged with 0.02 g (0.46 mmol) of anhydrous lithium chloride and 10 ml of THF. After cooling this solution to -78°C , 0.368 g (0.46 mmol) of $(\mu\text{-Ph}_3\text{SnS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$ in 10 ml of THF was cannulated into it. The mixture became brown and was stirred at -78°C for 30 min. It was then removed from the cold bath and stirred 4 h at room temperature. Removal of the solvent left a black tar which was extracted with pentane giving a red solution. This was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.031 g (0.069 mmol, 15% yield) of $(\mu\text{-SCH=CPHS})\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison of its ^1H NMR spectrum to that of an authentic sample.

References

1. Müller, A.; Jaegerman, W.; Enemark, J.H. Coord. Chem. Rev. 1982, 46, 245-280.
2. Vahrenkamp, H. Angew. Chem. Int. Ed. Engl. 1975, 14, 322.
3. Ginsberg, A.P.; Lindsell, W.E.; Sprinkle, C.R.; West, K.W.; Cohen, R.L. Inorg. Chem. 1982, 21, 3666-3681.
4. Braunstein, P.; Sappa, E.; Tiripicchio, A.; Camellini, M.T. Inorg. Chem. Acta 1980, 45, L191.
5. Brunner, H.; Wachter, J. J. Organomet. Chem. 1982, 240, C41.
6. Rauchfuss, T.B.; Weatherill, T.D.; Wilson, S.R.; Zebrowski, J.P. J. Am. Chem. Soc. 1983, 105, 6508.
7. Seyferth, D.; Henderson, R.S.; Fackler, J.P. Jr., Mazany, A.M. J. Organomet. Chem. 1981, 213, C21.
8. a) Seyferth, D.; Henderson, R.S.; Gallagher, M.K. J. Organomet. Chem. 1980, 193, C75.
b) Day, V.W.; Lesch, D.A.; Rauchfuss, T.B. J. Am. Chem. Soc. 1982, 104, 1290.
c) Braunstein, P.; Jud, J.M.; Tiripicchio, A.; Camellini, M.T.; Sappa, E. Angew. Chem. Int. Ed. Engl. 1982, 21, 307.
d) Braunstein, P.; Tiripicchio, A.; Camellini, M.T.; Sappa, E. Inorg. Chem. 1981, 20, 3586.
e) Williams, P.D.; Curtis, M.D.; Duffy, D.N.; Butler, W.M. Organometallics 1983, 2, 165.
f) Vahrenkamp, H.; Wucherer, E.J. Angew. Chem. Int. Ed. Engl. 1981, 20, 680.

- g) Khattab, S.A.; Markó, L.; Bor, G.; Markó, B. J. Organomet. Chem. 1964, 1, 373.
- h) Gallagher, M.K. Ph.D. dissertation, M.I.T., Cambridge, MA, 1984.
9. Clark, G.R.; Russell, D.R. J. Organomet. Chem. 1977, 136, Cl.
10. Farrar, D.H.; Grundy, K.R.; Payne, N.C.; Roper, W.R.; Walker, A. J. Am. Chem. Soc. 1979, 101, 6577.
11. Leonard, K.; Pluk, K.; Haltiwanger, R.C.; DuBois, M.R. Inorg. Chem. 1979, 18, 3246.
12. Coucouvanis, D.; Draganjac, M. J. Am. Chem. Soc. 1982, 104, 6820.
13. Giolando, D.M.; Rauchfuss, T.B. Organometallics 1984, 3, 487.
14. Bolinger, M.C.; Rauchfuss, T.B.; Rheingold, A.L. Organometallics 1982, 1, 1551.
15. Bolinger, M.C.; Rauchfuss, T.B. Inorg. Chem. 1982, 21, 3947.
16. Bolinger, M.C.; Rauchfuss, T.B.; Wilson, S.R. J. Am. Chem. Soc. 1981, 103, 5620.
17. Seyferth, D.; Henderson, R.S. J. Organomet. Chem. 1979, 182, C39.
18. a) Draganjac, M.; Coucouvanis, D. J. Am. Chem. Soc. 1983, 105, 139.
b) Halbert, T.R.; Pan, W.H.; Stiefel, E.I. J. Am. Chem. Soc. 1983, 105, 5476.

19. For other examples see:
- a) Bolinger, M.C.; Rauchfuss, T.B. J. Am. Chem. Soc. 1983, 105, 6321.
 - b) Halbert, T.R.; Pan, W.H.; Stiefel, E.I. J. Am. Chem. Soc. 1983, 105, 5476.
 - c) Migot, J.L.; Sala-Pala, J.; Guerchais, J.E. J. Organomet. Chem. 1983, 243, 427.
 - d) Kanatzidis, M.G.; Coucouvanis, D. Inorg. Chem. 1984, 23, 403.
20. a) Schumann, H.; Schmidt, M. Angew. Chem. Int. Ed. Engl. 1965, 4, 1007.
- b) Gladysz, J.A.; Wong, V.K.; Jick, B.S. Tetrahedron 1979, 35, 2329.
21. Reid, E.E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1958; Vol. 1, pp 37-38.
22. a) Jarvie, A.W.P.; Skelton, D. J. Organomet. Chem. 1971, 30, 145.
- b) Burton, H.; Davy, W.A. J. Chem. Soc. 1948, 528.
- c) Arnold, R.C.; Lien, A.P.; Alm, R.M. J. Am. Chem. Soc. 1950, 72, 731.
23. Seyferth, D.; Henderson, R.S.; Song, L.C. Organometallics 1982, 1, 125.
24. Seyferth, D.; Henderson, R.S. J. Am. Chem. Soc. 1979, 101, 508.
25. Haines, R.J.; DeBeer; J.A. J. Organomet. Chem. 1970, 24, 757.

26. Nametkin, N.S.; Tyurin, V.D.; Kukina, M.A. J. Organomet. Chem. 1978, 149, 355.
27. Dahl, L.F.; Wei, C.H. Inorg. Chem. 1963, 2, 328.
28. Henslee, W.; Davis, R.E. Cryst. Struct. Comm. 1972, 1, 403.
29. Shaver, A.; Fitzpatrick, P.J.; Steliou, K.; Butler, I.S. J. Am. Chem. Soc. 1979, 101, 1313.
30. King, R.B. J. Am. Chem. Soc. 1962, 84, 2460.
31. Seyferth, D.; Womack, G.B. J. Am. Chem. Soc. 1982, 104, 6839.
32. Silverstein, R.M.; Bassler, G.C.; Morrill, T.C. "Spectrometric Identification of Organic Compounds"; 4th ed.; Wiley: New York, 1981; p. 263.
33. See reference 32, p. 261.
34. Bird, C.W.; Hollins, E.M. J. Organomet. Chem. 1965, 4, 245.
35. Schrauzer, G.N.; Mayweg, V.P.; Heinrich, W. J. Am. Chem. Soc. 1966, 88, 4604.
36. The only asymmetric dithiolene $\text{Fe}_2(\text{CO})_6$ complex reported prior to this work was 7a reported in ref. 31.
37. Schrauzer, G.N.; Mayweg, V.P.; Heinrich, W. Inorg. Chem. 1965, 4, 1615.
38. Weber, H.P.; Brown, R.F. J. Chem. Soc. (A) 1967, 182.
39. Broadhurst, P.V.; Johnson, B.F.G.; Lewis, J.; Raithby, R.R. J. Chem. Soc., Chem. Comm. 1982, 140.
40. Glukhikh, V.I.; Yarosh, O.G.; Glukhikh, N.G.; Pensionerova, G.A.; Voronkov, M.G. Dokl. Akad. Nauk SSSR 1979, 247, 1405.

41. Kuivila, H.G.; Considine, J.L.; Sarma, R.H.; Mynott, R.J.
J. Organomet. Chem. 1976, 111, 179.
42. For other examples see:
- a) Mitchell, T.N.; Kummetat, C. J. Organomet. Chem.
1978, 157, 275.
- b) Mitchell, T.N.; Walter, G. J. Organomet. Chem.
1976, 121, 177.
43. Magnus, P.D.; Sarkar, T.; Djuric, S. "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F.G.A.; Abel, E.W.; Eds.; Pergamon Press: Oxford, England, 1982; Vol. 7. p. 519.
44. Carey, F.A.; Sundberg, R.J. "Advanced Organic Chemistry"; Plenum: New York, 1977; Part B, Chapter 1.
45. a) Streitwieser, A.; Ewing, S.P. J. Am. Chem. Soc. 1975, 97, 190.
- b) Streitwieser, A.; Williams, J.E. J. Am. Chem. Soc.
1975, 97, 192.
46. Campaigne, E. in "Organic Sulfur Compounds"; Kharash, N., Ed.; Pergamon Press: New York, 1961; Vol. 1, pp 134-140.
47. Seyferth, D.; Weiner, M.A.; Vaughan, L.G.; Raab, G.; Welch, D.E.; Cohen, H.M.; Alleston, D.L. Bull. Soc. Chim. France 1963, 1364.
48. Chieh, C.; Seyferth, D.; Song, L.-C. Organometallics
1982, 1, 473.
49. Skattebol, L.; Jones, E.R.H.; Whiting, M.C. Org. Syn.
1963, 4, 792.
50. Vick, S.J. Ph.D. dissertation, M.I.T., Cambridge, MA, 1977, p. 42.

51. a) Yamada, K.; Miyaaura, N. Itoh, M.; Suzuki, A.
Synthesis 1977, 679.
- b) Midland, M.M.; Tramontano, A.; Cable, J.R.
J. Organomet. Chem. 1980, 45, 28.
52. Gielen, M.; Nasielski, J. "Organotin Compounds"; Sawyer,
A.K.; Ed.; Marcel Dekker: New York, 1972; Vol. 3, p. 671.

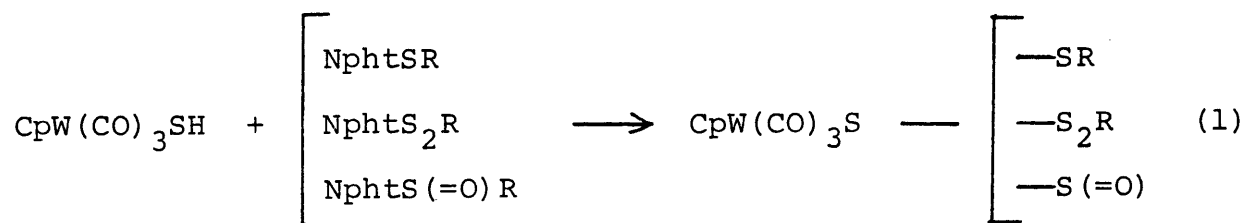
Chapter 2

The Reactivity of
(Di- μ -thiol)bis(tricarbonyliron)
Toward Electrophilic
Alkenes and Alkynes

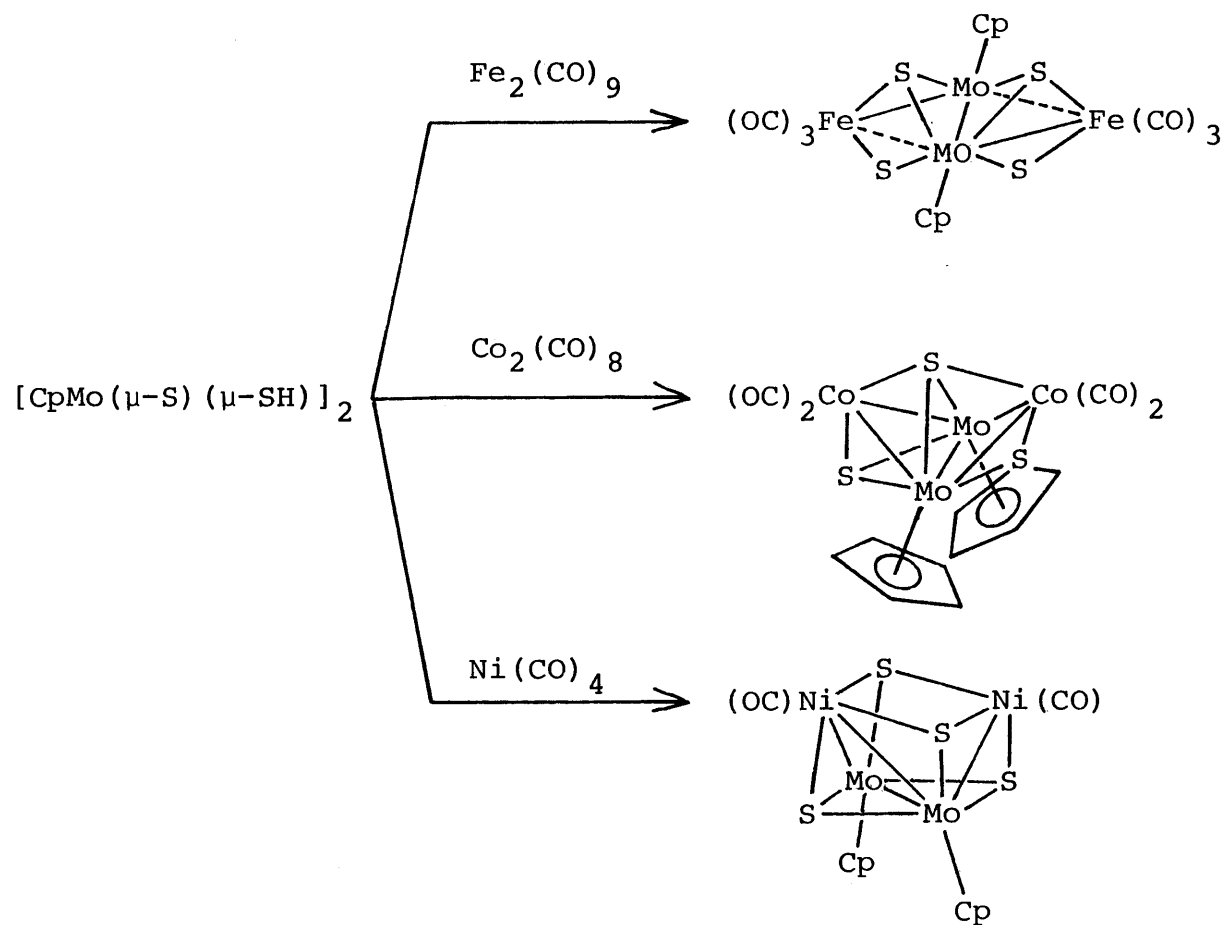
Introduction

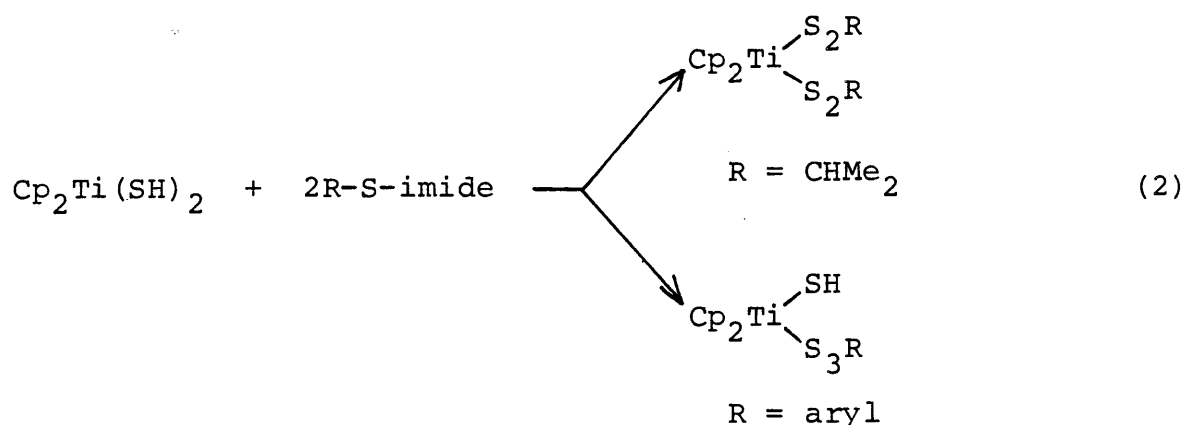
The recent study of sulfur-containing transition metal complexes has been stimulated by such diverse reasons as modeling of biologically important metal-sulfur proteins,¹ studying and modeling the hydrodesulfurization reaction,² and the synthesis of high nuclearity clusters.³ In this regard, attention has only recently been directed toward the thiol ligand as a potentially reactive site in transition metal complexes. The well-documented organic thiol chemistry provides ample precedent for believing inorganic thiol species will be reactive, useful synthetic reagents.⁴ Proof for this speculation has recently been appearing in the chemical literature. Curtis and Rakowski Dubois have demonstrated the use of transition metal thiol complexes in the synthesis of high nuclearity cluster compounds Scheme 1.^{5,6}

Reports have also appeared concerning the utilization of thiol ligands for the synthesis of new classes of organosulfur ligands. Taking a cue from organic thiol chemistry, Shaver and co-workers have shown that the thiol ligands of $\text{CpW}(\text{CO})_3\text{SH}$ and $\text{Cp}_2\text{Ti}(\text{SH})_2$ will react with sulfur transfer reagents of the type RS_x -imide (R = aryl and alkyl) to yield di- and trisulfano ligands, (eq.1 and 2).^{7,8} Angelici and co-workers have found



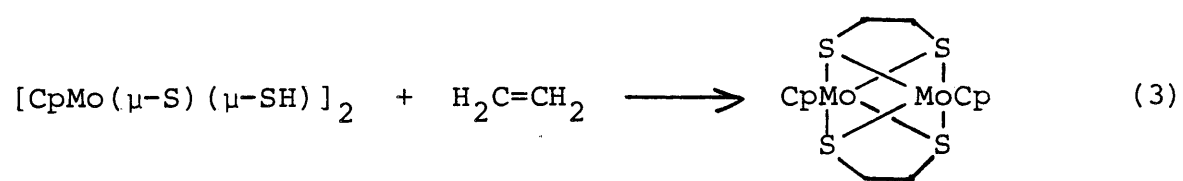
Scheme 1





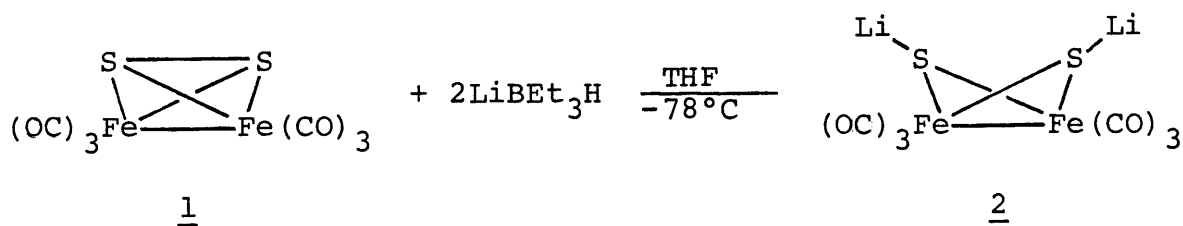
the SH ligand of $[(\text{CO})_5\text{WSH}]^-$ to be quite reactive toward a variety of organic electrophiles. Thus it reacted with selected ketones and aldehydes in the presence of $\text{F}_3\text{CSO}_3\text{H}$ to form coordinated thiolketones and thiolaldehydes⁹ it was also demonstrated to react with heterocumulenes yielding products resulting from thiol addition at the central carbon.¹⁰ Despite this willingness of $[\text{W}(\text{CO})_5\text{SH}]^-$ to react at carbon-element double bonds of heterocummulenes, it was reported not to have reacted with acetylenes or olefins, even the more electrophilic methyl acrylate, ethyl propiolate or acrylonitrile.

Another interesting thiol containing transition metal system, $[\text{CpMo}(\mu\text{-S})(\mu\text{-SH})]_2$, has been coming under the scrutiny of Rakowski Dubois and co-workers. This dinuclear complex has been reported to react with olefins, acetylenes and alkyl isocyanides but not by thiol addition reactions. Rather, the unsaturated molecules interact with the sulfido ligands followed by elimination of H_2 , (eq.3)^{2a,11}



Results and Discussion

While studying the reaction chemistry of μ -dithiobis(tricarbonyliron), 1, Henderson found that the sulfur-sulfur linkage of this molecule could be cleaved with reducing agents to form the sulfur-centered dianion $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2-}$, 2. Compound 2 was easily generated in THF at -78°C by the addition of two equivalents of LiBEt_3H to 1, resulting in a emerald green reaction mixture. Dianion 2 thus generated was allowed to react with a variety of metal and organic halides.^{3a} Quench-



ing 2 with trifluoroacetic acid at -78°C led to the isolation, in 98% yield, of di- μ -thiolbis(tricarbonyliron), 3, as a red, air sensitive, crystalline solid, Fig.1.¹² The ^1H NMR spectrum

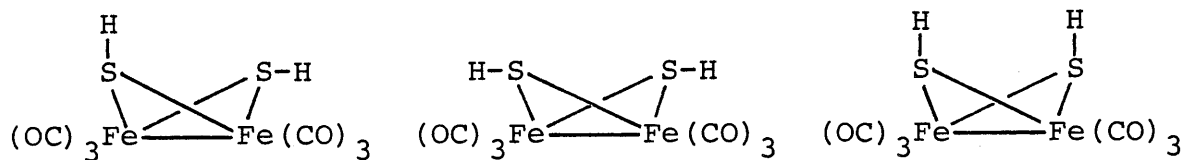
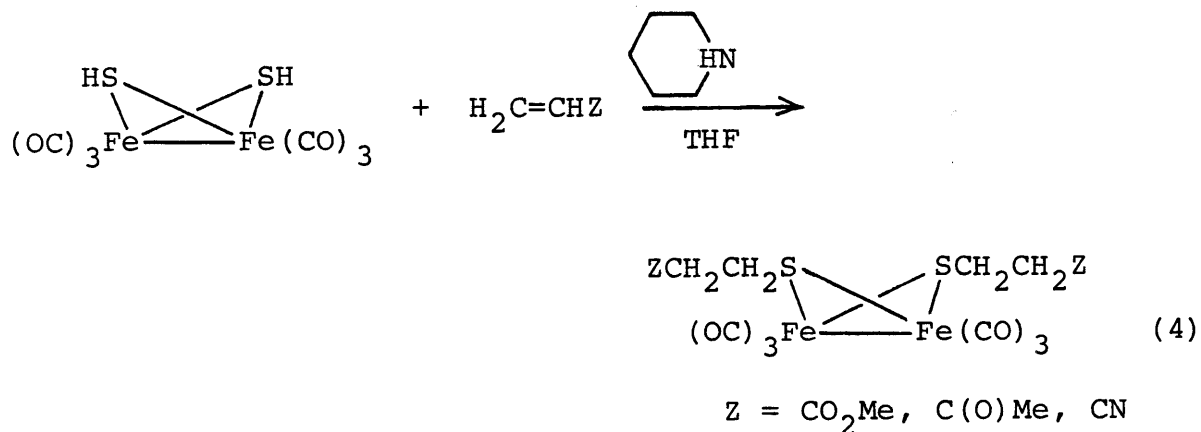


Figure 1: The three geometric isomers of 3.

of 3 indicated it to exist as a mixture of three isomers in a 14/2/1 (a,e/e, e/a,a) ratio. This is the only example of an a,a

isomer ever being observed for a $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ type complex. Apparently only hydrogen atoms are unrestricted sterically from forming this isomer.

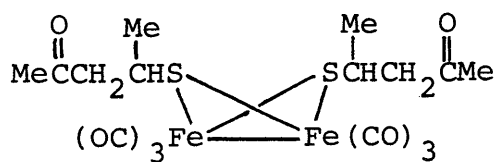
In an effort to study the chemistry of 3, Henderson found that it could be generated and used in-situ. Although not as extensively studied as dianion 2, $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ was found to undergo substitution reactions with alkylenedihalides and Me_2SnCl_2 in the presence of Et_3N , resulting in a bridging of the two sulfur atoms. It was also found that the thiol function of 3 could undergo Michael additions to methyl vinyl ketone, methyl acrylate and acrylonitrile.¹³ In the cases of methyl vinyl ketone and methyl acrylate, piperidine was used to catalyze the addition, (eq.4). In order to extend the



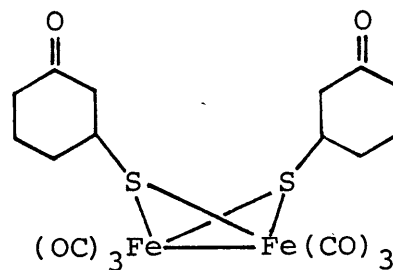
applicability of this reaction and explore its potential use for the synthesis of functionalized organosulfur ligands, 3 was allowed to react with a variety of α,β -unsaturated carbonyl compounds.

As had been observed previously for the terminally unsubstituted α,β -unsaturated carbonyl compounds (eq.4), those with

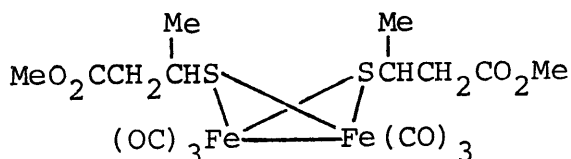
one substituent on the β carbon also afforded 2:1 adducts when allowed to react with 3 in the presence of piperidine. To perform these reactions a five fold excess of the carbonyl compound was added to the THF solution of 3 at -78°C , followed by the piperidine. The solution then was stirred for 0.5 h at -78°C and usually for 18 to 20 h after removal from the cold bath. Products were isolated and purified by column chromatography. Yields for the addition of the β substituted carbonyl compounds were lower than those obtained for the terminally unsubstituted ones. Thus trans-3-penten-2-one and 2-cyclohexenone gave compounds 4 and 5 in 62 and 70% yields, respectively. The α,β -unsaturated esters, methyl crotonate and diethyl maleate, gave even lower yields of the 2:1 adducts 6 (28%) and 7 (42%), respectively. None of these compounds



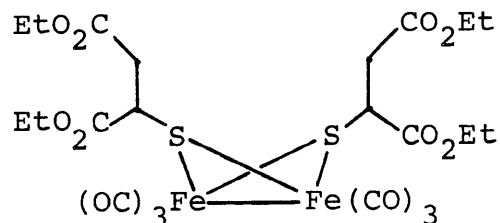
4



5



6



7

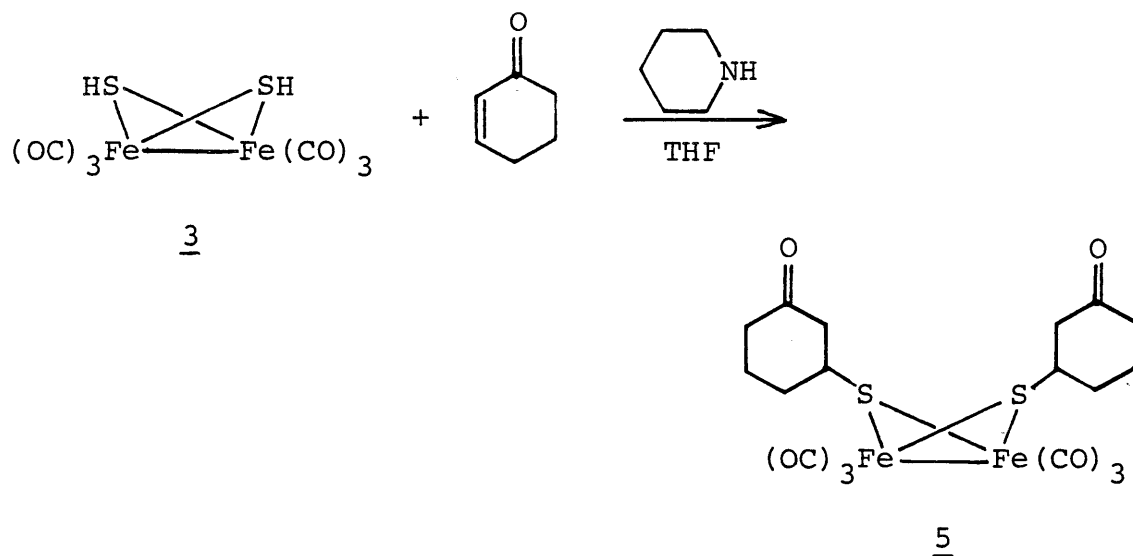
were crystalline; 4 and 6 were red oils, 5 a glassy solid and 7 an oily solid.

As μ -dialkylthiolatobis(tricarbonyliron) complexes, the aforementioned 2:1 adducts can exist as e,a and e,e isomers and were observed as such by ^1H and ^{13}C NMR spectroscopy. Complex 4, for example, displayed three singlets for the ketonic methyl groups in its 250MHz ^1H NMR spectrum which revealed an isomer ratio of 2.3/1.0 (e,a/e,e). For complex 5 the presence of both isomers was confirmed by means of its ^{13}C NMR (67.9MHz) spectrum which showed three ketonic carbonyl peaks at δ 204.3, 204.8 and 205.1. It was impossible to determine an isomer ratio for 7 due to the complexity of its ^1H NMR spectrum. Examination of the ester carbonyl region in its ^{13}C NMR spectrum revealed a multiplet at δ_{C} 169.6 attributed to the existence of isomers. Compound 6 was also isolated as a mixture of two isomers. The ^1H NMR spectrum revealed two OCH_3 signals at δ 3.57 and 3.65 indicating an isomer ratio of 3.8/1 (e,e/e,a).

In these reactions a nearly stoichiometric amount of piperidine was used although a catalytic amount will suffice. Table 1 reveals no significant yield differences between the use of a stoichiometric amount or 10 mole percent of base for the formation of 5.

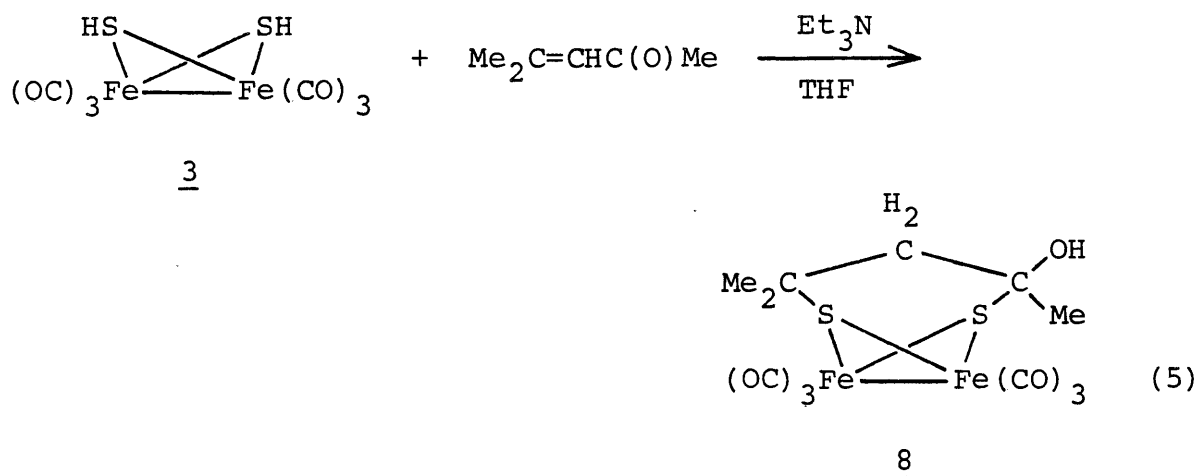
The reaction of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ with α,β -unsaturated ketones which had two alkyl substituents on the β -carbon resulted in the isolation of 1:1 adducts, (eq.5), despite the fact that a five fold excess of the ketone was used. This cyclization reaction is the result of SH addition to both

Table 1

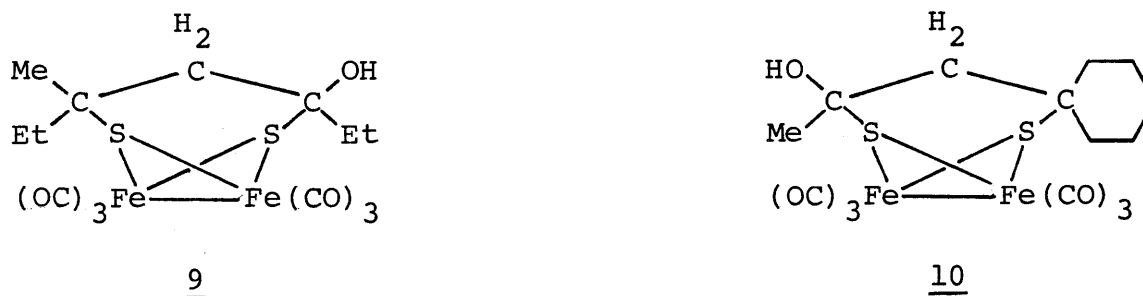


<u>mmol of 3^a</u>	<u>mmol of piperidine</u>	<u>% yield of 5</u>
2.91	6.06	61
2.91	5.05	70
2.91	0.06	59

^aUsing the standard procedure, 3 was generated in-situ from 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$.



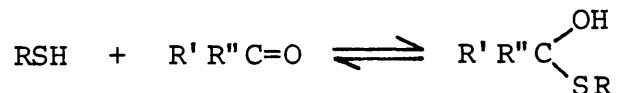
the C=C bond and carbonyl group. The alcohol, 8, was isolated by chromatography as an orange powder with a pungent, distasteful odor. Its IR spectrum revealed a hydroxy function but no ketonic carbonyl group. This material, however, proved difficult to purify so it was converted to the trimethylsilyl ether (via $(\text{Me}_3\text{Si})_2\text{NH}/\text{Me}_3\text{SiCl}$) which was an easily purified red, crystalline solid. The same bridging reaction was observed with $\text{Et}(\text{Me})\text{C}=\text{CHC}(\text{O})\text{Et}$ and cyclohexylideneacetone to give the alcohols 9 and 10 as red oils, which were also converted to the trimethyl-



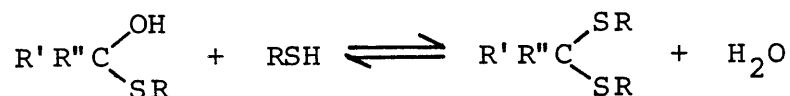
silyl ethers. The silyl ether of 9 was isolated as a 1 to 1 mixture of diastereomers. Another α,β -unsaturated ketone with

a disubstituted β carbon, 3-methyl-2-cyclohexenone, failed to give any isolable products after reacting with 3.

The syntheses of 8, 9, and 10 provide the only examples of a thiol group of 3 adding to an organic carbonyl function. This addition allowed the isolation of cyclic hemithioketal complexes of $\text{Fe}_2(\text{CO})_6$. Examples of organic hemithioketals and hemithioacetals stable enough to isolate are not plentiful but do exist, generally when electron-withdrawing groups are present in the carbonyl compound.^{14,15} Thiols add more readily to the carbonyl function than the corresponding alcohols; the addition is reversible with the location of the equilibrium dependent on the nature of the aldehyde or ketone and thiol.^{14,16}



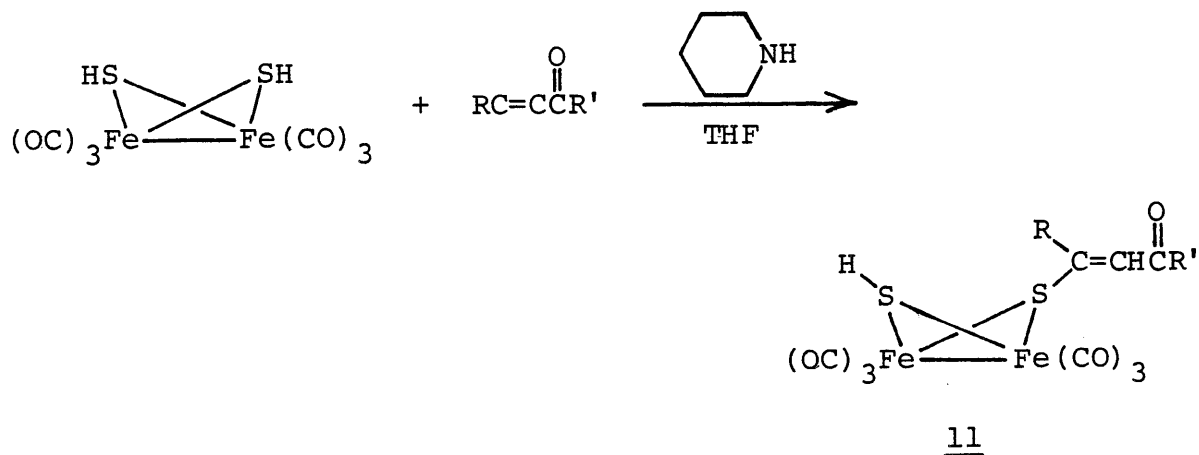
In the presence of an acid catalyst the α -hydroxy sulfide will react with a second thiol to produce the thioketal or thioacetal.¹⁷ Hoping that 3 would under go a similar reaction,



Henderson attempted the *p*-toluenesulfonic acid catalyzed addition of 3 to benzophenone but reported that it failed.¹⁸ Acetone also failed to react with 3 using piperidine as the catalyst.

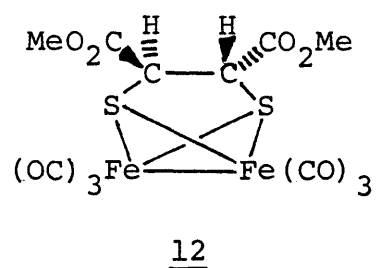
Three-carbon bridged addition products of α,β -unsaturated ketones were isolated only when the β carbon was fully substituted. This being the case, 3 was allowed to react with $\text{Me}_2\text{C}=\text{CHCO}_2\text{Me}$, an α,β -unsaturated ester with a disubstituted β carbon. The reaction, however, failed, so that the hoped for bridging thioester could not be isolated. The use of one equivalent of methyl vinyl ketone, rather than an excess, did not force the production of the hemithioketal product. Rather the 2:1 adduct was isolated in 28% yield.

Acetylenes conjugated to a carbonyl group were found to react with 3 to yield 1:1 adducts resulting from two consecutive Michael additions. The first addition would result in a vinyl derivative, 11. In such a complex, the two thio ligands



are in close proximity to one another, as in the a,e isomer of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ in which the S---S distance is 2.93\AA ,¹⁹ such that intramolecular addition of the remaining HS function to the vinyl group should be very favorable. Addition of the second HS function to form either a one- or two-carbon bridge

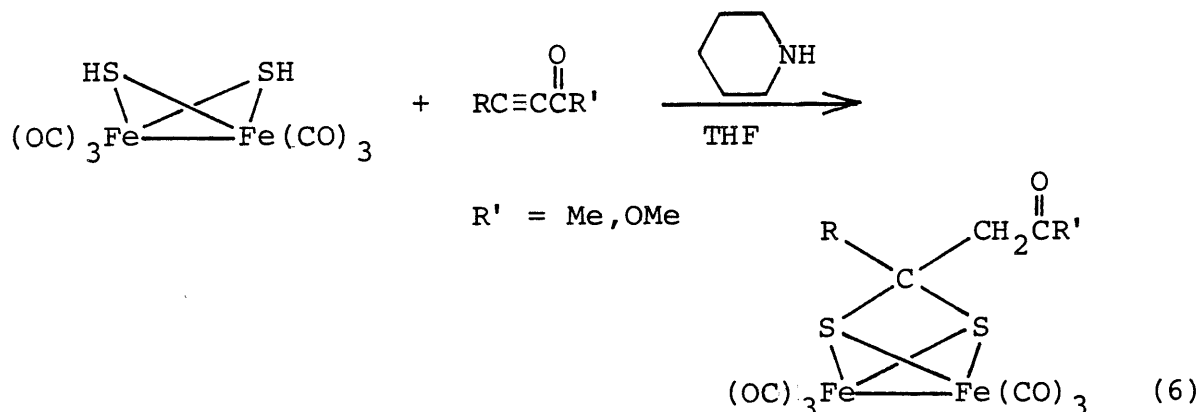
between the two sulfur atoms depended on R. When R was a group capable of stabilizing the negative charge generated in the base catalyzed addition of the thiol, as in the case of dimethyl acetylenedicarboxylate, the second -SH addition occurred to yield a two-carbon bridged product, 12, in 68% yield, mp 119-120°C. Identification of 12 as the two-carbon



bridged product was confirmed by the fact that the carboxylate methyl groups were equivalent in the proton NMR spectrum at δ 3.77 and the bridge carbons were equivalent in the ^{13}C NMR spectrum at δ_{C} 54.9. Although this information was in agreement with the structure of 12, it did not reveal the orientation of the carboxylate groups as being cis or trans to each other. With regard to this problem, Shaver had previously shown that unsymmetric groups bridging the $\text{S}_2\text{Fe}_2(\text{CO})_6$ frame could make the $\text{Fe}(\text{CO})_3$ groups inequivalent in ^{13}C NMR spectra.²⁰ This discovery indicated that the $\text{Fe}(\text{CO})_3$ groups of such compounds are independently fluxional. In the case of 10, if the carboxylate groups were cis to one another, the $\text{Fe}(\text{CO})_3$ units would be inequivalent. However, since the ^{13}C NMR spectrum (CDCl_3 , 67.9MHz) shows a singlet at δ_{C} 206.9 for the

iron carbonyls, it indicates the $\text{Fe}(\text{CO})_3$ units to be equivalent. This favors the trans isomer, 12, for which just such an observation is expected.

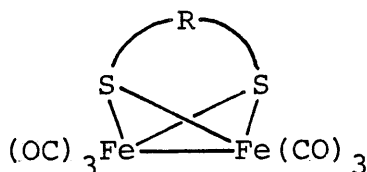
Other acetylenes studied did not have two activating groups conjugated to the olefin. In these cases one-carbon bridged complexes were the sole products, (eq.6), resulting




from two Michael additions directed to the β carbon. The structures of these compounds were established on the basis of ^1H and ^{13}C NMR spectroscopy, Table 2. The structural assignment of these compounds is best illustrated by discussing the $\text{MeC} \equiv \text{CC}(\text{O})\text{Me}$ addition product, 13, formed in 42% yield. Its isomeric alternative would be 14. The ^1H NMR spectrum (CDCl_3 ,



Table 2. ^1H and ^{13}C NMR Data for Alkylene-Bridged Derivatives of $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$.

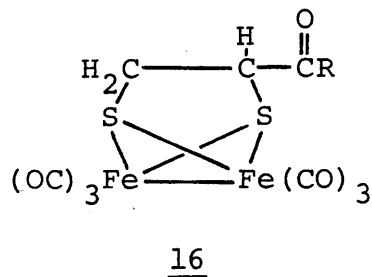
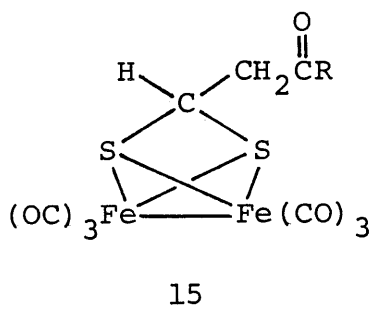


NO	Bridge (R)	δ		
		Bridge Protons	Bridge Carbons	Iron Carbonyls
1	CH_2	4.64	63.35 ^a	209.3
2	CH_2CH_2^b	2.45	36.29	208.23
3	$\text{MeO}_2\text{CHCHCO}_2\text{Me}$	3.71	54.9	206.9
4	$\text{CHCH}_2\text{CO}_2\text{Me}$	5.07	72.6	208.0, 208.4
5	$\text{CHCH}_2\text{C(O)Me}$	5.02	72.3	208.0, 208.2
6	$\text{MeCCH}_2\text{C(O)Me}$	-	82.3	208.1, 208.2
7	$\text{Me}_2\text{CCH}_2\text{C(OSiMe}_3\text{)Me}$	-	77.9, 57.0, 37.7	207.9, 208.2
8	 $\text{CCH}_2\text{C(OSiMe}_3\text{)Me}$	-	77.7, 54.9, 41.4	208.0, 208.3

^aShaver, A.; Fitzpatrick, P.J.; Steliou, K.; Butler, I.S.; J. Am. Chem. Soc., 1979, 101, 1313.

^bGallagher, M.K. Ph.D. dissertation, M.I.T., Cambridge, MA, 1981, p. 141.

90MHz) shows only three singlets at δ 1.89 (3H), 2.13 (3H) and 3.21 (2H) in harmony with 13 and contrary to what would be expected for 14. The ^{13}C NMR spectrum (CDCl_3 , 67.9MHz) again could only be attributed to 13 due to the absence of any doublets in the proton-coupled spectrum; δ_{C} 30.7 (q, $J = 128\text{Hz}$, CH_3), 38.1 (q, $J = 132\text{Hz}$, $\text{C}(\text{O})\underline{\text{CH}}_3$), 62.7 (t, $J = 128\text{Hz}$, CH_2), 82.3 (s, S-C-S), 201.8 (s, ketone $\text{C}=\text{O}$), 208.1 and 208.2 (s, $\text{Fe}(\text{CO})_3$). It is reasonable to assume that the addition products resulting from $\text{HC}\equiv\text{CC}(\text{O})\text{R}$ ($\text{R} = \text{Me}, \text{OMe}$) also have the methylene-bridged structure. Table 2 shows the similarity of the chemical shifts for the bridge protons and carbons of these two compounds (entries 4 and 5) to the simple methylene-bridged species (entry 1), as opposed to the ethylene-bridged complex (entry 2). It should also be noted that if the $\text{HC}\equiv\text{CC}(\text{O})\text{R}$ acetylenes gave two-carbon bridged products, 16, the presence of a chiral carbon could give rise to diastereotopic methylene groups and hence more complicated proton NMR spectra than were observed. Unambiguous proof of structure 15 ($\text{R} = \text{Me}$) was pro-



vided by an X-ray structure determination, Fig.2.²¹

Compound 15 ($\text{R} = \text{Me}$) crystallized in the space group C2/c

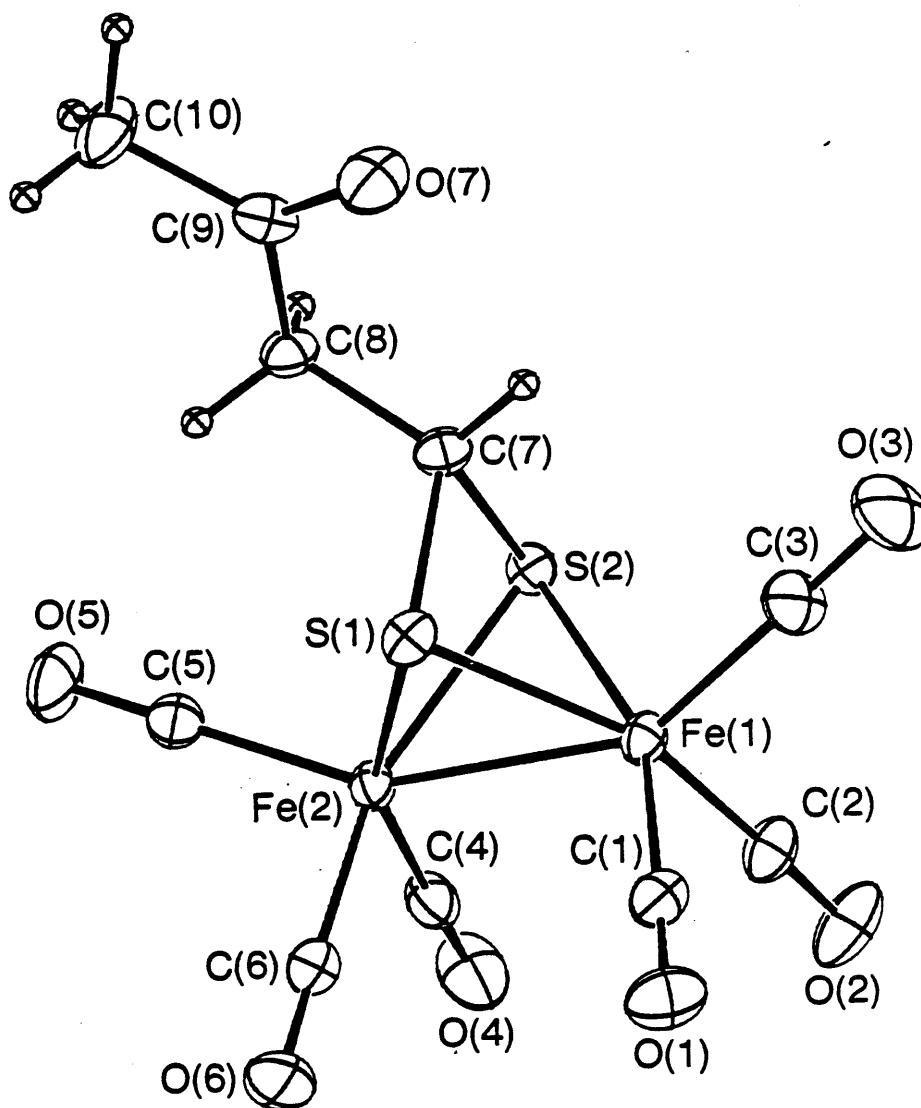


Figure 2. Perspective drawing of $(\mu\text{-CH}_3\text{C(O)CH}_2\text{CHS}_2)\text{Fe}_2(\text{CO})_6$, 15. Thermal ellipsoids are drawn at the 20% probability level except for hydrogens which are drawn artificially small.

Table 3. Selected Bond Lengths (Å) for $(\mu\text{-CH}_3\text{C}(\text{O})\text{CH}_2\text{CHS}_2)\text{Fe}_2(\text{CO})_6$.

Fe(1)-Fe(2)	2.4847(12)	Fe(1)-C(1)	1.797(7)
Fe(1)-S(1)	2.2575(18)	Fe(1)-C(2)	1.796(8)
Fe(1)-S(2)	2.2703(17)	Fe(1)-C(3)	1.795(7)
Fe(2)-S(1)	2.2761(17)	Fe(2)-C(4)	1.794(7)
Fe(2)-S(2)	2.2571(17)	Fe(2)-C(5)	1.809(7)
S(1)-C(7)	1.835(6)	Fe(2)-C(6)	1.796(8)
C(7)-S(2)	1.836(6)	C(1)-O(1)	1.136(8)
C(7)-C(8)	1.512(9)	C(2)-O(2)	1.127(8)
C(8)-C(9)	1.499(8)	C(3)-O(3)	1.144(8)
C(9)-C(10)	1.472(10)	C(4)-O(4)	1.133(8)
C(9)-O(7)	1.206(7)	C(5)-O(5)	1.126(8)
		C(6)-O(6)	1.137(8)

Table 4. Selected Angles (deg) in $(\mu\text{-CH}_3\text{C(O)CH}_2\text{CHS}_2)\text{Fe}_2(\text{CO})_6$.

C(3)-Fe(1)-C(2)	99.6(3)	C(4)-Fe(2)-C(6)	91.9(3)
C(3)-Fe(1)-C(1)	98.9(3)	C(4)-Fe(2)-C(5)	96.6(3)
C(3)-Fe(1)-S(1)	102.4(3)	C(4)-Fe(2)-S(1)	156.6(2)
C(3)-Fe(1)-Fe(2)	150.2(2)	C(4)-Fe(2)-Fe(1)	100.3(2)
C(3)-Fe(1)-S(2)	98.6(2)	C(4)-Fe(2)-S(2)	94.2(2)
C(2)-Fe(1)-C(1)	91.5(3)	C(6)-Fe(2)-C(5)	100.0(3)
C(2)-Fe(1)-S(1)	156.3(2)	C(6)-Fe(2)-S(2)	156.4(2)
C(2)-Fe(1)-S(2)	96.3(2)	C(6)-Fe(2)-S(1)	98.1(2)
C(2)-Fe(1)-Fe(2)	99.0(2)	C(6)-Fe(2)-Fe(1)	99.5(2)
C(1)-Fe(1)-S(1)	93.5(2)	C(5)-Fe(2)-S(2)	101.9(2)
C(1)-Fe(1)-S(2)	159.4(2)	C(5)-Fe(2)-S(1)	104.6(2)
C(1)-Fe(1)-Fe(2)	103.5(2)	C(5)-Fe(2)-Fe(1)	153.7(2)
S(1)-Fe(1)-Fe(2)	57.12(5)	S(2)-Fe(2)-Fe(1)	56.97(5)
S(2)-Fe(1)-Fe(2)	56.46(5)	S(1)-Fe(2)-Fe(1)	56.41(5)
C(7)-S(1)-Fe(1)	88.3(2)	C(7)-S(2)-Fe(2)	90.3(2)
C(7)-S(1)-Fe(2)	89.7(2)	C(7)-S(2)-Fe(1)	87.9(2)
Fe(1)-S(1)-Fe(2)	66.47(5)	Fe(2)-S(2)-Fe(1)	66.57(5)
Fe(1)-C(1)-O(1)	179.0(6)	C(8)-C(7)-S(2)	117.7(4)
Fe(1)-C(2)-O(2)	177.9(7)	C(8)-C(7)-S(1)	116.1(4)
Fe(1)-C(3)-O(3)	177.5(7)	S(1)-C(7)-S(2)	92.9(3)
Fe(2)-C(4)-O(4)	179.2(6)	C(9)-C(8)-C(7)	112.5(5)
Fe(2)-C(5)-O(5)	177.0(6)	O(7)-C(9)-C(10)	120.9(6)
Fe(2)-C(6)-O(6)	178.5(7)	O(7)-C(9)-C(8)	121.9(6)
		C(10)-C(9)-C(8)	117.2(6)

with eight molecules in the unit cell, which has dimensions $a = 15.378(2)\text{\AA}$, $b = 9.6620(9)\text{\AA}$, $c = 21.768(3)\text{\AA}$, $\beta = 108.23(1)^\circ$, and $V = 3072.0\text{\AA}^3$. The structural features of this compound are very similar to those of the simple methylene analog, $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$, which have been reported by Shaver, et al.²² Thus the $\text{S}_2\text{C(H)CH}_2\text{C(O)CH}_3$ ligand functions as a six-electron donor with both sulfur atoms bound to both metals. The sulfur and iron atoms are arranged in a butterfly-type structure. The $\text{S}(1)\text{-Fe}(1)\text{-S}(2)$ angle is compressed by 9.0° in comparison to $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ due to the alkylene bridge.¹⁹ Also notable is the acute $\text{S}(1)\text{-C}(7)\text{-S}(2)$ angle of $92.9(3)^\circ$ indicating significant strain in this part of the molecule. A plane bisecting the Fe-Fe bond and directed through $\text{S}(1)$, $\text{C}(7)$ and $\text{S}(2)$ clearly shows that the two $\text{Fe}(\text{CO})_3$ units are inequivalent and hence distinguishable by ^{13}C NMR spectroscopy.

Table 2 also presents the chemical shifts of the iron-carbonyl carbons and bridge carbons for various bridged $\text{S}_2\text{Fe}_2(\text{CO})_6$ derivatives. Those compounds with symmetric bridging groups, entries 1,2,3, have a single peak for the iron carbonyls indicating the equivalency and fluxional behavior of the two $\text{Fe}(\text{CO})_3$ groups. However, for bridges which result in inequivalent $\text{Fe}(\text{CO})_3$ groups, entries 4 through 8, the ^{13}C NMR spectra reveal this inequivalency by showing two iron-carbonyl signals. This supports the suggestion of Shaver that the two $\text{Fe}(\text{CO})_3$ groups in alkyl derivatives of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ are independently fluxional.

Clearly these results indicate that the ligated thiol

function can be a useful reactive site in transition metal complexes. In the present study the thiol ligands of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ were found to undergo Michael additions to various α,β -unsaturated carbonyl compounds, which proved to be a useful synthesis of functionalized organic thio ligands. Due to the proximity of the two thiol functions, bridging reactions also occurred if the α,β -unsaturated compound had two sites susceptible to thiol addition. This occurred for the α,β -unsaturated ketones with two substituents on the β carbon forming three carbon bridges between the sulfur atoms by thiol addition to both the C=C bond and carbonyl function. Acetylenes conjugated to a carbonyl group also reacted with 3 to produce dithiolate ligands by two consecutive Michael additions to the $\text{C}\equiv\text{C}$ bond.

Experimental Section

General Comments

All reactions were carried out under an atmosphere of pre-purified tank nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Diethyl ether was distilled from lithium aluminum hydride. Reagent grade pentane and dichloromethane were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Filtration chromatography, in which the reactions products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 ml) in a 350 ml glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration. Column chromatographies were performed with a 350 x 250 mm column using either silicic acid or Florisil (Fisher, 100-200 mesh). All chromatographies were done under atmospheric conditions; all solid products were recrystallized from deoxygenated solvents at -20°C.

Infrared spectra were obtained using a Perkin-Elmer Model 457A or Model 283 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60, JeolFX-90Q or Bruker 250 NMR spectrometers operating at 60MHz, 90MHz, and 250MHz, respectively. ¹³C NMR spectra were obtained using a JeolFX-90Q or Bruker 270 instrument operating at 22.5MHz and 67.9MHz, respectively. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70eV. Melting points were determined on analytically pure samples using a Büchi Capillary Melting Point Apparatus

and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Isomers of the $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ type complexes were determined by the integration of the appropriate signals in the ^1H NMR spectra. $(\mu\text{-Dithio})\text{bis}(\text{tricarbonyliron})$ was synthesized using a literature procedure.^{3a}

In-Situ Preparation of $(\mu\text{-Dithiol})\text{bis}(\text{tricarbonyl})$.

A dry, three-necked, 300 ml round-bottomed flask equipped with a stir-bar and serum caps was charged with 1.0 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and flushed with nitrogen. THF (50 ml) was added by syringe and the solution cooled to -78°C . To this solution 6.0 ml (6.0 mmol) of 1M LiBEt_3H in THF (Aldrich) was added, resulting in a red to green color change. After stirring for 15 min, 0.46 ml (6.0 mmol) of F_3CCOOH (Baker) was added by syringe causing a color change to red. This solution was stirred for 10 min before further reactants were added.

Reaction Between $(\text{Di-}\mu\text{-thiol})\text{bis}(\text{tricarbonyliron})$ and trans-3-Penten-2-one. (GBW-III-6, GBW-IV-38).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$, at -78°C was utilized. By syringe, 1.46 ml (15 mmol) of trans-3-penten-2-one (Aldrich) was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was subjected to filtration chromatography (silicic acid/ CH_2Cl_2). Dichloro-

methane eluted a red band which yielded a red oil (1.27 g) that was then applied to column chromatography (silicic acid/CH₂Cl₂). Dichloromethane/pentane (3/1, v/v) eluted a yellow band (trace of brown solid, not identified), an orange band (0.118 g of red oil, mixture (by NMR) of product and organic impurities), and a red band which yielded 0.928 g (1.81 mmol, 62% yield) of (μ -CH₃C(O)CH₂C(CH₃)HS)₂Fe₂(CO)₆ as a slightly air sensitive red oil, identified as a mixture of two isomers, 2.3/1 (e,a/-e,e).

IR (CHCl₃): 2965(m), 2925(m), 2899(sh), 2870(sh), 1715(s) (C=O), 1449(m), 1409(m), 1362(s), 1305(m), 1155(s), 1105(m), 1024(m), 964(m), 912(s), 615(m), 551(m) cm⁻¹;

terminal carbonyl region (CHCl₃): 2071(s), 2035(vs), 1990(vs) cm⁻¹.

¹H NMR (CDCl₃, 250MHz): δ 2.10, 2.13 (both s, a,e isomer, C(O)CH₃), 2.15 (s, e,e isomer, C(O)CH₃), 3.0-2.46 (m), 1.39-1.31 (m) and 1.13 (d, J = 6.4Hz) [HC(CH₃)CH₂].

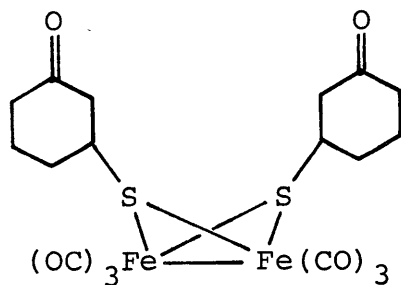
Mass spectrum, m/z (relative intensity): 430 (M⁺-3CO, 56), 402 (M⁺-4CO, 14), 374 (M⁺-5CO, 14), 346 (M⁺-6CO, 100), 261 (Fe₂S₂OC₅H₉, 42), 176 (Fe₂S₂, 70), 144 (Fe₂S, 14), 112 (Fe₂, 14), 88 (SFe, 84), 56 (Fe, 56).

Anal. Calcd. for C₁₆H₁₈Fe₂O₈S₂: C, 37.38; H, 3.53%.

Found: C, 37.46; H, 3.68%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and 2-Cyclohexenone. (GBW-II-69).

The standard in-situ preparation of 2.91 mmol of (μ -HS)₂-Fe₂(CO)₆ at -78°C was utilized. By syringe, 1.50 ml (15.0 mmol) of 2-cyclohexenone (Aldrich) was added to the solution at -78°C, followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was left in the cold bath and allowed to warm overnight to room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was subjected to filtration chromatography (silicic acid/CH₂Cl₂). Dichloromethane eluted a red band which yielded a red oil. An application to column chromatography (silicic acid/CH₂Cl₂) of this oil gave a minor orange band (not identified) and a red band which yielded 1.09 g (2.02 mmol, 70% yield) of an air-stable, red glassy solid, mp 102°C dec, identified as:



IR (CHCl₃): 2953(m), 2875(m), 1710(s) (C=O), 1445(m), 1413(m), 1342(m), 1313(m), 1280(m), 1171(m), 1090(m), 1054(m), 1032(m), 968(m), 909(m), 877(m), 558(m) cm⁻¹;

terminal carbonyl region (CDCl₃): 2078(s), 2044(vs), 1995(vs) cm⁻¹.

^1H NMR (CDCl_3 , 60MHz): δ 2.5-1.4 (m).

^{13}C $\{^1\text{H}\}$ (C_6D_6 , 67.9MHz): δ_{C} 23.5, 33.7, 35.4, 39.5, 48.6, 49.3 (ring carbons), 204.3, 204.8, 205.1 (organic CO, e,e and e,a isomers) and 208.6 (s, CO).

Mass spectrum, m/z (relative intensity): 454 (M^+-3CO , 3), 426 (M^+-4CO , 3), 398 (M^+-5CO , 3), 370 (M^+-6CO , 20), 273 ($\text{Fe}_2\text{S}_2\text{C}_6\text{H}_9\text{O}$, 20), 176 (Fe_2S_2 , 24), 112 (FeS , 10), 97 ($\text{C}_6\text{H}_9\text{O}$, 48), 56 (Fe, 100).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{Fe}_2\text{O}_8\text{S}_2$: C, 40.17; H, 3.37%.

Found: C, 40.02; H, 3.61%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Methyl Crotonate. (GBW-III-4).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.60 ml (15 mmol) of methyl crotonate (Aldrich) was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was left in the cold bath and allowed to warm overnight to room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was subjected to filtration chromatography (silicic acid/ CH_2Cl_2). Diethyl ether/ CH_2Cl_2 (1/4, v/v) eluted a red-brown band which yielded a brown oil. Application to column chromatography (silicic acid/ CH_2Cl_2) of this oil gave a red band which yielded 0.439 g (0.80 mmol, 28% yield) of $(\mu\text{-CH}_3\text{O-C(O)CH}_2\text{C(CH}_3\text{)HS})_2\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, viscous red oil. It was identified as a mixture of two isomers, 3.8/1

(e,e/e,a), by its ^1H NMR spectrum.

IR (CHCl_3): 2949(m), 2920(m), 2850(m), 1727(s) (C=O), 1432 (m), 1351(m), 1302(m), 1255(s), 1195(s), 1092(m), 1014(m), 919(w), 707(vs), 671(s), 603(s), 578(s), 549(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2060(s), 2041(vs), 1998(vs) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 1.05 to 1.60 and 2.10-2.80 (both m, $\text{HC}(\text{CH}_3)\text{CH}_2$), 3.57 and 3.65 (both s, OCH_3).

Mass spectrum, m/z (relative intensity): 462 (M^+-3CO , 6), 434 (M^+-4CO , 18), 406 (M^+-5CO , 30), 378 (M^+-6CO , 100), 277 ($\text{Fe}_2\text{S}_2-\text{C}_5\text{H}_9\text{O}_2$, 36), 112 (Fe_2 , 30), 88 (FeS , 18), 56 (Fe , 24).

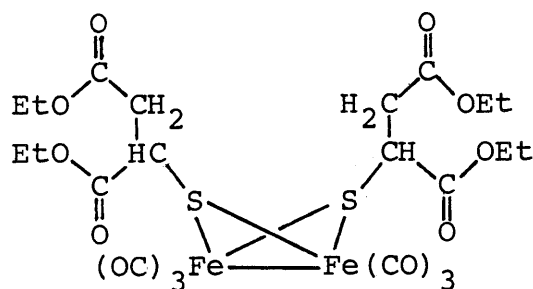
Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{Fe}_2\text{O}_{10}\text{S}_2$: C, 35.19; H, 3.32%.

Found: C, 34.66; H, 3.42%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Diethyl Maleate. (GBW-II-64, GBW-IV-50).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 2.42 ml (15 mmol) of diethyl maleate (Eastman) was added, followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was left in the cold bath and allowed to warm overnight to room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was subjected to filtration chromatography (silicic acid/ CH_2Cl_2). Dichloromethane/hexane (1/1, v/v) eluted a minor red-brown band which gave a brown oily residue (not identified); CH_2Cl_2 eluted a minor red band

which gave 0.24 g of a red oil (not identified) and $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (4/1, v/v) moved a red band which yielded a red oil (2.69 g). The diethyl maleate was removed from this oil by short path distillation at reduced pressure (0.1 mmHg) using an oil bath not exceeding 75°C. The remaining red oil was then applied to column chromatography (silicic acid/ CH_2Cl_2). Dichloromethane moved a red band which yielded 0.846 g (1.23 mmol, 42% yield) of a slightly air-sensitive, red oily solid identified as:



IR (CHCl_3): 2989(s), 2941(m), 2910(m), 2878(w), 1730(s) (C=O), 1473(sh), 1463(m), 1444(m), 1404(m), 1392(m), 1370(s), 1200 (s, broad), 1135(m), 1109(m), 1038(s), 909(m), 896(sh), 857(m), 617(m), 562(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2084(s), 2050(vs), 2010(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.42-1.21 (m, 12H, CH_3), 4.34 to 4.07 (m, 8H, OCH_2), 3.4 to 2.3 (m, 12H, CH_2 -CH).

Mass spectrum FD: M^+ (690), calcd. (690.26).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 67.9MHz): δ_{C} 13.7, 33.0, 38.9, 39.3, 47.3, 60.9, 61.1, 61.7, 62.2 (organic carbons), 169.6 (m, ester CO), 207.5 (s, CO).

Anal. Calcd. for $C_{22}H_{26}Fe_2O_{14}S_2$: C, 38.28; H, 3.80%.

Found: C, 38.79; H, 4.01%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Mesityl Oxide. (GBW-II-26, GBW-II-51).

The standard in-situ preparation of 2.91 mmol of $(\mu-HS)_2-Fe_2(CO)_6$ at $-78^\circ C$ was utilized. By syringe, 1.70 ml (15.0 mmol) of mesityl oxide was added to the solution at $-78^\circ C$, followed by the addition of 0.7 ml (5.03 mmol) of Et_3N (Baker). The reaction mixture was stirred 0.5 h at $-78^\circ C$ and 18 h at room temperature. The solvent was removed by a trap-to-trap distillation leaving a brown oil which was applied to filtration chromatography (silicic acid/ Et_2O). Diethyl ether eluted an orange band which gave 1.04 g (2.35 mmol, 81% yield) of $(\mu-SC(OH)(CH_3)CH_2C(CH_3)_2S)Fe_2(CO)_6$, as a slightly air-sensitive, orange-brown solid with a pungent, distasteful odor (resembling that described for thioacetone).

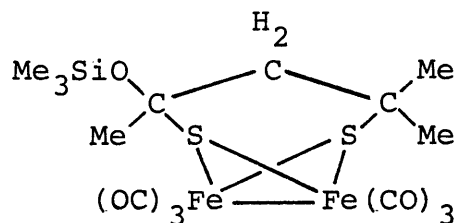
IR ($CHCl_3$): 3585(s) (O-H), 3360(m, broad) (O-H), 2968(m), 2929(m), 2890(w), 2875(w), 1442(m), 1415(w), 1366(s), 1310(m), 1280(m), 1262(w), 1178(m), 1133(s), 1059(m), 1007(w), 994(w), 951(m), 936(m), 900(w), 859(m), 606(m), 565(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2084(s), 2043(vs), 2000(vs) cm^{-1} .

Since an analytically pure sample of the alcohol could not be obtained, the trimethylsilyl ether was prepared for characterization (GBW-II-58).

A 100 ml, three-necked, round-bottomed flask equipped

with a stir-bar, serum caps and a 50 ml pressure-equalizing addition funnel was charged with 0.60 g (1.35 mmol) of the above alcohol and flushed with nitrogen. THF (30 ml) and three drops of trimethylchlorosilane (Petrach) were added. Hexamethyldisilazane (Petrach), 6.74 ml (32.3 mmol) and 5 ml of THF were added to the addition funnel. This solution was added dropwise to the alcohol solution. The resulting mixture then was stirred for 20 h. The solvent was removed leaving a black solid which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted an orange band which yielded 0.572 g (1.10 mmol, 82% yield) of an air-stable red solid, mp 90-91°C after crystallization from pentane, identified as:



IR (CHCl_3): 2969(m), 2935(m), 2880(sh), 1465(sh), 1443(m), 1412(w), 1374(m), 1365(m), 1354(w), 1280(m), 1255(m), 1162(m), 1135(s), 1090(s), 1064(m), 1013(m), 997(m), 968(s), 941(w), 923(w), 893(m), 850(s), 613(m), 570(m) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2083(s), 2045(vs), 2012(vs), 1994(sh) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.21 (s, 9H, SiCH_3), 1.63, 1.38, 1.24, (all s, 9H, CH_3), 1.82 and 1.30 (AX quartet, $J = 15.2\text{Hz}$, 2H, CH_2).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 2.4 (q, $J = 119\text{Hz}$, SiCH_3), 31.7 (q, $J = 128\text{Hz}$, CH_3), 35.6 (q, $J = 128\text{Hz}$, CH_3), 35.9 (q, $J = 130\text{Hz}$, CH_3), 37.7 (s, CMe_2), 57.0 (t, $J = 127\text{Hz}$, CH_2), 77.9 (s, $\text{C}(\text{OSiMe}_3)(\text{Me})$), 207.9 and 208.2 (both s, CO).

Mass spectrum, m/z (relative intensity): 516 (M^+ , 1), 460 ($\text{M}^+ - 2\text{CO}$, 3), 432 ($\text{M}^+ - 3\text{CO}$, 8), 376 ($\text{M}^+ - 5\text{CO}$, 23), 348 ($\text{M}^+ - 6\text{CO}$, 81), 258 ($\text{Fe}_2\text{S}_2\text{C}_6\text{H}_{10}$, 20), 176 (Fe_2S_2 , 44), 172 ($\text{C}_{12}\text{H}_{20}\text{OSi}$, 47), 144 (Fe_2S , 10), 112 (Fe_2 , 24), 73 (SiMe_3 , 100), 56 (Fe, 100).

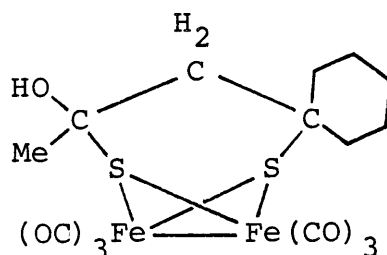
Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{Fe}_2\text{O}_7\text{S}_2\text{Si}$: C, 34.90; H, 3.91%.

Found: C, 34.89; H, 3.97%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Cyclohexylideneacetone.²³ (GBW-IV-59).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 3.0 g (16 mmol) of cyclohexylideneacetone²³ (as a mixture of α,β and β,γ isomers, 74% α,β by ^1H NMR) was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and for 6.5 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (1/1, v/v) eluted a minor brown band (not collected) and CH_2Cl_2 eluted a red band which gave 1.48 g of a red oil. This was applied to column chromatography (silicic acid/ CH_2Cl_2). Dichloromethane eluted a red band which yielded 1.04 g (2.15

mmol, 74% yield) of a red tar identified as:



IR (CHCl_3): 3579(s) (O-H), 3350(s, broad) (O-H), 2932(s), 2860(m), 1443(s), 1369(m), 1307(w), 1294(m), 1140(m), 1114(w), 1097(w), 1064(m), 1007(w), 983(w), 946(m), 909(w), 854(m), 838(m), 610(sh), 564(m) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2085(s), 2055(s), 2015(s), 2000(sh) cm^{-1} .

To facilitate the characterization of this alcohol, the trimethylsilyl ether was prepared according to the following procedure (GBW-IV-61).


To 1.0 g (2.06 mmol) of the above alcohol in 40 ml of THF, four drops of Me_3SiCl and 8.51 ml (40.8 mmol) of hexamethyldisilazane (Petrach) were added. The reaction mixture was stirred for 20 h. Removal of the solvent left a brown tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.50 g (0.90 mmol, 44% yield) of an air-stable red solid identified as the silylated alcohol, mp 85-86°C after crystallization from pentane. Further elution with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1/4, v/v) moved a red band which gave 0.274 g (0.57 mmol, 28% yield)

of the starting alcohol. Identification of the silylated product was based on the following data:

IR (CHCl_3): 2935(s), 2861(m), 1441(m), 1371(w), 1294(w), 1253(s), 1135(m), 1105(s), 1078(m), 1057(s), 989(m), 970(s), 913(m), 885(s), 844(s), 610(sh), 565(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2075(s), 2037(vs), 2000(vs), 1990(sh) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.20 (s, 9H, SiCH_3), 2.06, 1.15 (AXq, $J = 15.0\text{Hz}$, 2H, CH_2), 1.24 to 1.63 (m, 13H, ring protons and CH_3).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 2.29 (q, $J = 119\text{Hz}$, SiCH_3), 21.8 (t, $J = 127\text{Hz}$, CH_2), 22.2 (t, $J = 127\text{Hz}$, CH_2), 25.7 (t, $J = 130\text{Hz}$, CH_2), 35.6 (q, $J = 128\text{Hz}$, CH_3), 39.9 (t, $J = 126\text{Hz}$, CH_2), 41.4 (s, C ) , 43.3 (t, $J = 113\text{Hz}$, CH_2), 54.9 (t, $J = 127\text{Hz}$, CH_2), 77.7 (s, $\text{CMe}(\text{OSiMe}_3)$), 208.0 and 208.3 (both s, CO).

Mass spectrum, m/z (relative intensity): 500 ($\text{M}^+ - 2\text{CO}$, 1), 472 ($\text{M}^+ - 3\text{CO}$, 8), 444 ($\text{M}^+ - 4\text{CO}$, 1), 416 ($\text{M}^+ - 5\text{CO}$, 32), 388 ($\text{M}^+ - 6\text{CO}$, 87), 298 ($\text{Fe}_2\text{S}_2\text{C}_9\text{H}_{14}$, 31), 212 ($\text{C}_{12}\text{H}_{24}\text{OSi}$, 100), 176 (Fe_2S_2 , 1), 144 (Fe_2S , 7), 112 (Fe_2 , 8), 73 (SiMe_3 , 8), 56 (Fe, 3).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{Fe}_2\text{O}_7\text{S}_2\text{Si}$: C, 38.86; H, 4.35%.

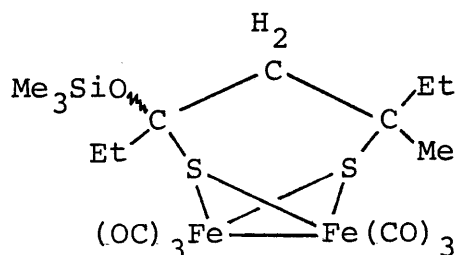
Found: C, 39.01; H, 4.41%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and 5-Methyl-4-Hepten-3-one.²⁴ (GBW-IV-65).

The standard in-situ preparation of 2.91 mmol of

$(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 30 mmol of 5-methyl-4-hepten-3-one²⁴ (6.10 g of a mixture of α,β and β,γ isomers, 62% α,β by ^1H NMR) was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was stirred for 0.5 h at -78°C and for 6.5 h at room temperature. The solvent was removed by a trap-to-trap distillation. The remaining red oil was applied to filtration chromatography (silicic acid/ CH_2Cl_2) twice which gave a red oil, containing the desired product, extremely contaminated with the starting ketone.

Since we were unable to purify the alcohol product, the trimethylsilyl ether was prepared (GBW-IV-65). To the above red oil in 40 ml of THF, four drops of Me_3SiCl and 8.5 ml (40.8 mmol) of hexamethyldisilazane were added. The reaction mixture was stirred for 45 h. Removal of the solvent left a brown oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted an orange band which gave 0.49 g (0.90 mmol, 31% yield based on $\text{S}_2\text{Fe}_2(\text{CO})_6$) of an air-stable, red solid, mp $58\text{--}61^\circ\text{C}$ after crystallization from pentane. It was identified as a 1:1 mixture of diastereomers of:



IR (CHCl_3): 2955(s), 2920(sh), 2882(sh), 1450(m), 1378(m),

1353(w), 1329(w), 1254(s), 1176(m), 1155(m), 1089(s), 1050(m), 1000(m), 975(m), 949(w), 906(s), 845(s), 561(m), cm^{-1} ;

terminal carbonyl region (CHCl_3): 2067(s), 2030(vs), 1999(s), 1992(sh) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.21, 0.22 (both s, 9H, SiCH_3), 8.7 to 2.0 (m, 15H, all other protons).

Mass spectrum, m/z (relative intensity): 404 ($\text{M}^+ - 5\text{CO}$, 5), 376 ($\text{M}^+ - 6\text{CO}$, 32), 286 ($\text{Fe}_2\text{S}_2\text{C}_8\text{H}_{14}$, 32), 176 (Fe_2S_2 , 15), 144 (Fe_2S , 15), 112 (Fe_2 , 3), 88 (FeS , 2), 73 (SiMe_3 , 100), 56 (Fe , 16).

Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{Fe}_2\text{O}_7\text{S}_2\text{Si}$: C, 37.51; H, 4.44%.

Found: C, 37.60; H, 4.40%.

Attempted Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and 3-Methyl-2-cyclohexen-1-one.²⁵ (GBW-IV-47).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.65 g (15 mmol) of 3-methyl-2-cyclohexen-1-one²⁵ was added at -78°C followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was taken up in Et_2O and filtered through a pad of silicic acid. Removal of the solvent left a red brown oil, TLC analysis of which showed five minor spots. The IR spectrum of this material showed no bands for either hydroxy or organic carbonyl functions. In view of

these results the material was not worked with further.

Attempted Reaction Between (Di- μ -thiol)bis(tricarbonyliron)
and Acetone. (GBW-V-6).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.10 ml (15 mmol) of acetone was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was stirred for 0.5 h at -78°C and 23 h at room temperature. The reaction solution was added to 50 ml of a 5% HCl solution which was then extracted with Et_2O . The Et_2O layer was separated and dried over MgSO_4 . After filtration the solvent was removed leaving a trace amount of a black tarry residue.

Attempted Reaction Between (Di- μ -thiol)bis(tricarbonyliron)
and Methyl 3-methyl-2-butenolate.²⁶ (GBW-V-13).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.71 g (15 mmol) of methyl 3-methyl-2-butenolate²⁶ was added to the solution at -78°C , followed by the addition of 0.5 ml (5.05 mmol) of piperidine. The reaction mixture was stirred for 0.5 h at -78°C and 20 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane) but no products eluted from the column.

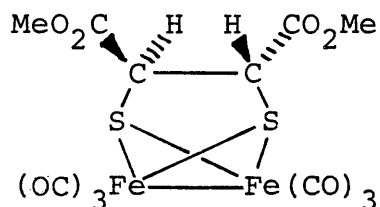
Reaction Between (Di- μ -thiol)bis(tricarbonyliron), and One Equivalent of Methyl Vinyl Ketone. (GBW-X-66).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 0.25 ml (3.0 mmol) of methyl vinyl ketone (Aldrich) was added at -78°C followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and for 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (1/1, v/v) eluted a minor orange band which gave 0.15 g of a red tar. This material could not be identified but its IR spectrum showed no bands due to a hydroxy function. Diethyl ether eluted a red band which yielded 0.40 g (0.82 mmol, 28% yield) of $(\mu\text{-MeC(O)CH}_2\text{CH}_2\text{S})_2\text{Fe}_2(\text{CO})_6$ as a dark red oil, identified by comparison of its IR, ^1H NMR and mass spectra to those of an authentic sample.²⁷

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Dimethylacetylene Dicarboxylate. (GBW-II-39).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.84 ml (15 mmol) of dimethylacetylene dicarboxylate was added to the solution at -78°C , followed by 0.7 ml (5.03 mmol) of Et_3N (Baker). The reaction mixture was stirred for 0.5 h at -78°C and 4.5 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown tar which was applied to filtration

chromatography (silicic acid/ CH_2Cl_2). Dichloromethane eluted a red band which yielded 0.96 g (1.97 mmol, 68% yield) of an air-stable, red solid, mp 119-120°C after crystallization from CH_2Cl_2 /pentane, identified as:



IR (CHCl_3): 2964(m), 2858(w), 1735(s) (C=O), 1436(m), 1300(m), 1270(s, broad), 1209(s), 1007(m), 909(w), 894(w), 613(m), 562(s) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2093(s), 2055(vs), 2020(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 3.77 (s, 6H, OCH_3), 3.71 (s, 2H, CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 53.1 (q, $J = 148\text{Hz}$, CH_3), 54.9 (d, $J = 147\text{Hz}$, CH), 169 (s, ester carbonyl), 206.9 (s, CO).

Mass spectrum, m/z (relative intensity): 432 ($\text{M}^+ - 2\text{CO}$, 1), 404 ($\text{M}^+ - 3\text{CO}$, 1), 376 ($\text{M}^+ - 4\text{CO}$, 4), 348 ($\text{M}^+ - 5\text{CO}$, 6), 320 ($\text{M}^+ - 6\text{CO}$, 41), 176 (Fe_2S_2 , 100), 144 (Fe_2S , 8), 112 (Fe_2 , 4), 88 (FeS , 4), 56 (Fe, 14).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{Fe}_2\text{O}_{10}\text{S}_2$: C, 29.53; H, 1.65%.

Found: C, 29.68; H, 1.70%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and Methyl Propiolate. (GBW-III-1).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ at -78°C was utilized. By syringe, 1.30 ml (15 mmol) of methyl propiolate (Aldrich) was added, followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was filtered through a pad of silica gel (Fischer, 200 mesh). Removal of the solvent from the red filtrate left a red oil which was subjected to column chromatography (silicic acid/ CH_2Cl_2). Methylene chloride eluted a red band which yielded 0.589 g (1.37 mmol, 47% yield) of $(\mu\text{-CH}_3\text{OC(O)CH}_2\text{CHS}_2)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, red oil.

IR (CHCl_3): 2949(m), 2842(w), 1734(s) (C=O), 1437(m), 1405(w), 1353(s), 1277(m), 1165(m), 1114(w), 1010(w), 987(m), 943(m), 901(w), 849(w), 609(sh), 559(m) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2065(s), 2024(vs), 1996(vs) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 3.00 (d, $J = 7.2\text{Hz}$, 2H, CH_2), 3.63 (s, 3H, OCH_3) and 5.07 (t, $J = 7.2\text{Hz}$, 1H, CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 47.4 (t, $J = 131\text{Hz}$, CH_2), 52.0 (q, $J = 147\text{Hz}$, OCH_3), 72.6 (d, $J = 161\text{Hz}$, S_2CH), 168.4 (s, ester CO), 208.2 and 208.4 (both s, CO).

Mass spectrum, m/z (relative intensity): 402 ($M^+ - CO$, 1), 374 ($M^+ - 2CO$, 19), 346 ($M^+ - 3CO$, 18), 318 ($M^+ - 4CO$, 17), 290 ($M^+ - 5CO$, 25), 262 ($M^+ - 6CO$, 100), 176 (Fe_2S_2 , 74), 144 (Fe_2S , 22), 112 (Fe_2 , 2), 56 (Fe , 7).

Anal. Calcd. for $C_{10}H_6Fe_2O_8S_2$: C, 27.93; H, 1.41%.

Found: C, 28.32; H, 1.59%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and 3-Butyn-2-one. (BGW-III-36).

The standard in-situ preparation of 2.91 mmol of $(\mu-HS)_2-Fe_2(CO)_6$ was utilized. By syringe, 1.17 ml (15 mmol) of 3-butyn-2-one (Farchan) was added, followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at $-78^\circ C$ and for 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was taken up in CH_2Cl_2 and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to column chromatography (silicic acid/ CH_2Cl_2). Dichloromethane eluted a red band which yielded 0.533 g (1.29 mmol, 44% yield) of $(\mu-CH_3C(O)CH_2CHS_2)-Fe_2(CO)_6$ as an air-stable red solid, mp $90-91^\circ C$ after crystallization from pentane/ CH_2Cl_2 .

IR ($CHCl_3$): 2940(w), 2895(sh), 1716(s) ($C=O$), 1398(m), 1360(s), 1338(m), 1183(sh), 1159(s), 1114(sh), 1066(m), 1019(m), 974(w), 659(m) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2079(s), 2039(vs), 1996(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 2.10 (s, 3H, CH_3), 3.08 (d, $J = 6.5\text{Hz}$, 2H, CH_2) and 5.02 (t, $J = 6.5\text{Hz}$, 1H, CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 30.0 (q, $J = 128\text{Hz}$, CH_3), 56.3 (t, $J = 128\text{Hz}$, CH_2), 72.3 (d, $J = 160\text{Hz}$, CH), 201.9 (s, ketonic CO), 208.0 and 208.4 (both s, CO).

Mass spectrum, m/z (relative intensity): 358 ($\text{M}^+ - 2\text{CO}$, 10), 330 ($\text{M}^+ - 3\text{CO}$, 10), 302 ($\text{M}^+ - 4\text{CO}$, 5), 274 ($\text{M}^+ - 5\text{CO}$, 10), 246 ($\text{M}^+ - 6\text{CO}$, 25), 176 (Fe_2S_2 , 45), 144 (Fe_2S , 15), 112 (Fe_2 , 5), 88 (FeS , 10), 56 (Fe, 100).

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{Fe}_2\text{O}_7\text{S}_2$: C, 29.01; H, 1.46%.

Found: C, 29.12; H, 1.57%.

Reaction Between (Di- μ -thiol)bis(tricarbonyliron) and 3-Pentyn-2-one.²⁸ (GBW-V-4).

The standard in-situ preparation of 2.91 mmol of $(\mu\text{-HS})_2\text{-Fe}_2(\text{CO})_6$ was utilized. By syringe, 1.23 ml (15 mmol) of 3-pentyn-2-one²⁸ was added, followed by the addition of 0.5 ml (5.05 mmol) of piperidine (Aldrich). The reaction mixture was stirred for 0.5 h at -78°C and for 18 h at room temperature. The solvent was removed on a rotary evaporator leaving a brown oil which was taken up in CH_2Cl_2 and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to column chromatography (silicic acid/ CH_2Cl_2). Pentane/ CH_2Cl_2 (2/1, v/v) eluted a minor brown band which was not collected, followed by a red band. The silicic acid was removed from the column and the red band was extracted from it with CH_2Cl_2 . Removal of the solvent yielded 0.508 g

(1.21 mmol, 42% yield) of $(\mu\text{-CH}_3\text{C(O)CH}_2\text{C(CH}_3)_2\text{S}_2)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, red oil.

IR (CHCl_3): 2961(m), 2930(m), 2870(sh), 1710(s) (C=O), 1400(m), 1357(s), 1319(s), 1262(m), 1160(s), 1087(m), 968(m), 908(m), 864(w), 821(w) cm^{-1} ;

terminal carbonyl region (CHCl_3): 2080(s), 2040(vs), 2011(vs), 1993(sh) cm^{-1} .

^1H NMR (CDCl_3 , 60MHz): δ 1.89 (s, 3H, $-\text{CH}_3$), 2.13 (s, 3H, CH_3), 3.21 (s, 2H, CH_2).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 30.7 (q, $J = 128\text{Hz}$, CH_3), 38.1 (q, $J = 132\text{Hz}$, CH_3), 62.7 (t, $J = 128\text{Hz}$, CH_2), 82.3 (s, S-C-S), 202.2 (s, ketonic CO), 208.1 and 208.2 (both s, CO).

Mass spectrum, m/z (relative intensity): 372 ($\text{M}^+ - 2\text{CO}$, 8), 344 ($\text{M}^+ - 3\text{CO}$, 12), 316 ($\text{M}^+ - 4\text{CO}$, 12), 288 ($\text{M}^+ - 5\text{CO}$, 12), 260 ($\text{M}^+ - 6\text{CO}$, 72), 176 (S_2Fe_2 , 100), 144 (SFe_2 , 28), 112 (Fe_2 , 16), 88 (SFe , 4), 56 (Fe , 100).

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{Fe}_2\text{O}_7\text{S}_2$: C, 30.87; H, 1.88%.

Found: C, 30.80; H, 2.01%.

References

1. a) Stiefel, E.I. Prog. Inorg. Chem. 1977, 22, 1.
b) Holm, R.H. Accounts Chem. Res. 1977, 10, 427.
2. a) DuBois, M.R.; Van Derveer, M.C., DuBois, D.L.;
Haltiwanger, R.C.; Miller, W.K. J. Am. Chem. Soc.
1980, 102, 7456.
b) DuBois, M.R. J. Am. Chem. Soc. 1983, 105, 3710.
3. a) Seyferth, D.; Henderson, R.S.; Song, L.-C.
Organometallics 1982, 1, 125.
b) Rauchfuss, T.B.; Weatherill, T.D.; Wilson, S.R.;
Zebrowski, J.P. J. Am. Chem. Soc. 1983, 105, 6508.
c) Vahrenkamp, H. Angew. Chem. Int. Ed. Engl. 1975,
14, 322.
4. Patai, S., ed. "The Chemistry of the Thiol Group"; Part 1
and 2, Wiley-Interscience: New York, 1974.
5. Curtis, M.D.; Williams, P.D. Inorg. Chem. 1983, 22,
2661.
6. Cowans, B.; Noordik, J.; DuBois, M.R. Organometallics
1983, 2, 938.
7. Shaver, A.; Hartzlerink, J.; Lai, R.D.; Bird, P.; Ansari,
A. Organometallics 1983, 2, 938.
8. Shaver, A.; McCall, J.M.; Bird, P.H.; Ansari, N.
Organometallics 1983, 2, 1894.
9. Gingerich, R.G.W.; Angelici, R.J. J. Am. Chem. Soc.
1979, 101, 5604.
10. Angelici, R.J.; Gingerich, G.W. Organometallics 1983,
2, 89.

11. DuBois, D.L.; Miller, W.K.; DuBois, M.R. J. Am. Chem. Soc. 1981, 103, 3429.
12. Seyferth, D.; Henderson, R.S.; Song, L.-C. J. Organomet. Chem. 1980, 192, C1.
13. Seyferth, D.; Henderson, R.S. J. Organomet. Chem. 1981, 218, C34.
14. Reid, E.E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1960; Vol. 3, pp 320-330.
15. Field, L.; Sweetman, B.J. J. Org. Chem. 1969, 1799.
16. Campaigne, E. in "Organic Sulfur Compounds"; Kharasch, N., Ed.; Pergamon Press: New York, 1961; Vol. 1, pp 134-140.
17. Kumar, V.; Dev, S. Tet. Let. 1983, 24, 1289.
18. Henderson, R.S. Ph.D. dissertation, M.I.T., Cambridge, MA, 1981, p. 117.
19. Dahl, L.F.; Wei, C.H. Inorg. Chem. 1963, 2, 328.
20. Shaver, A.; Fitzpatrick, P.J.; Steliou, K.; Butler, I.S. J. Organomet. Chem. 1979, 172, C59.
21. Seyferth, D.; Womack, G.B.; Song, L.-C.; Cowie, M.; Hames, B.W. Organometallics 1983, 2, 928.
22. Shaver, A.; Fitzpatrick, P.J.; Steliou, K.; Butler, I.S. J. Am. Chem. Soc. 1979, 101, 1313.
23. Jupp, L.G.; Kon, G.A.R.; Lockton, E.H. J. Chem. Soc. 1928, 1638.
24. Abbott, A.E.; Kon, G.A.R.; Satchell, R.D. J. Chem. Soc. 1928, 2514.
25. Cronyn, M.W.; Riesser, G.H. J. Am. Chem. Soc. 1953, 75, 1664.

26. Halmos, V.M.; Mahacsi, T. J. Prakt. Chem. 1960, 12, 50.
27. Henderson, R.S. Ph.D. dissertation, M.I.T., Cambridge, MA, 1981, p. 115.
28. Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: New York, 1971; p. 81.

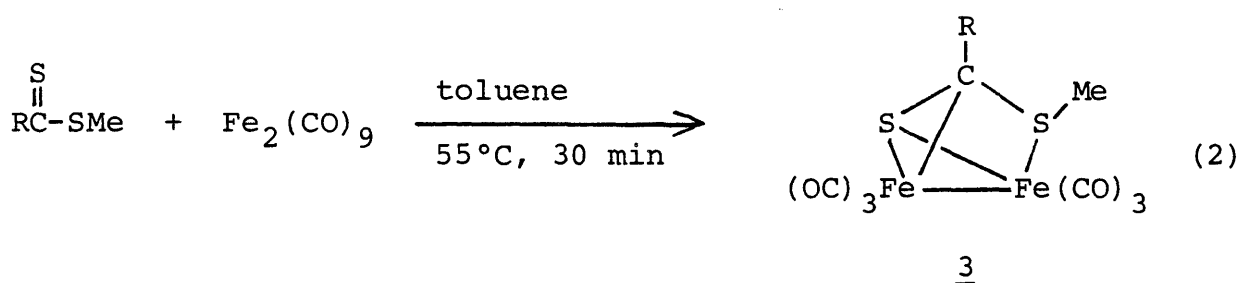
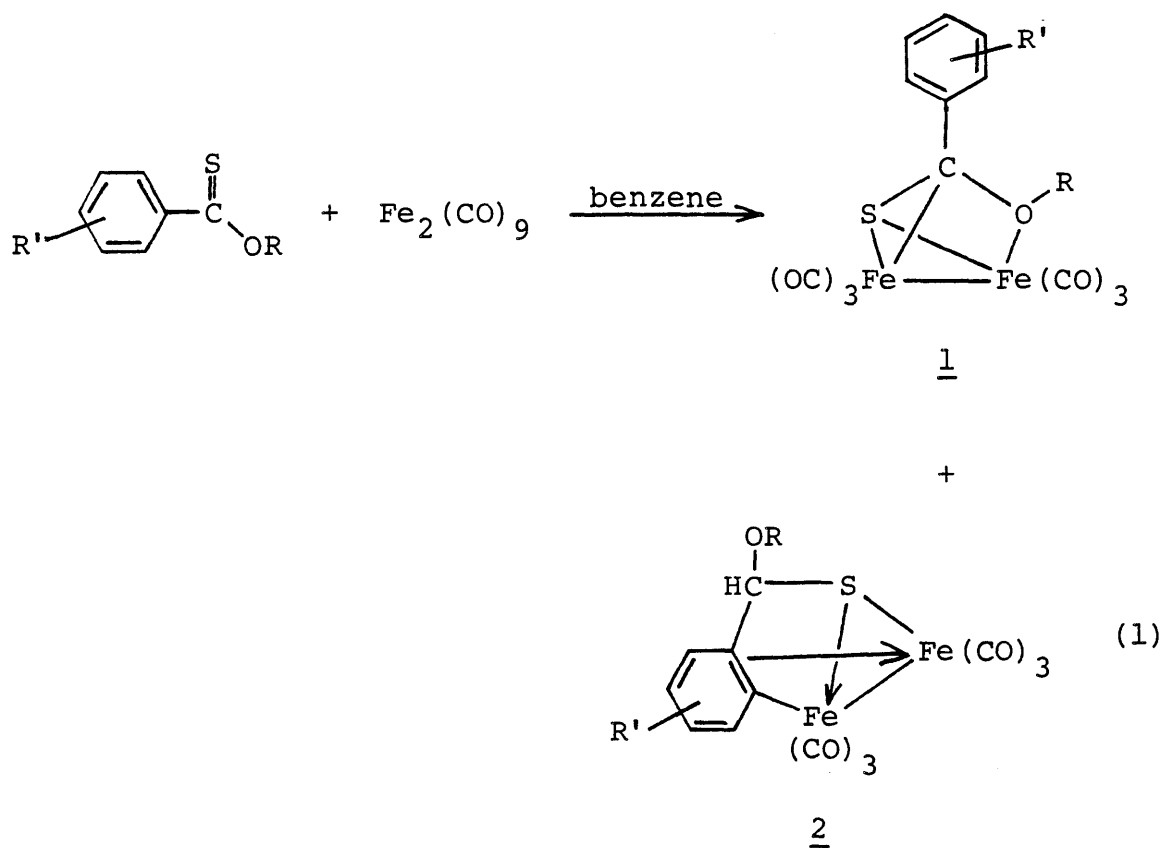
Chapter 3

Diiron Hexacarbonyl Complexes of
Thioesters and Dithioesters

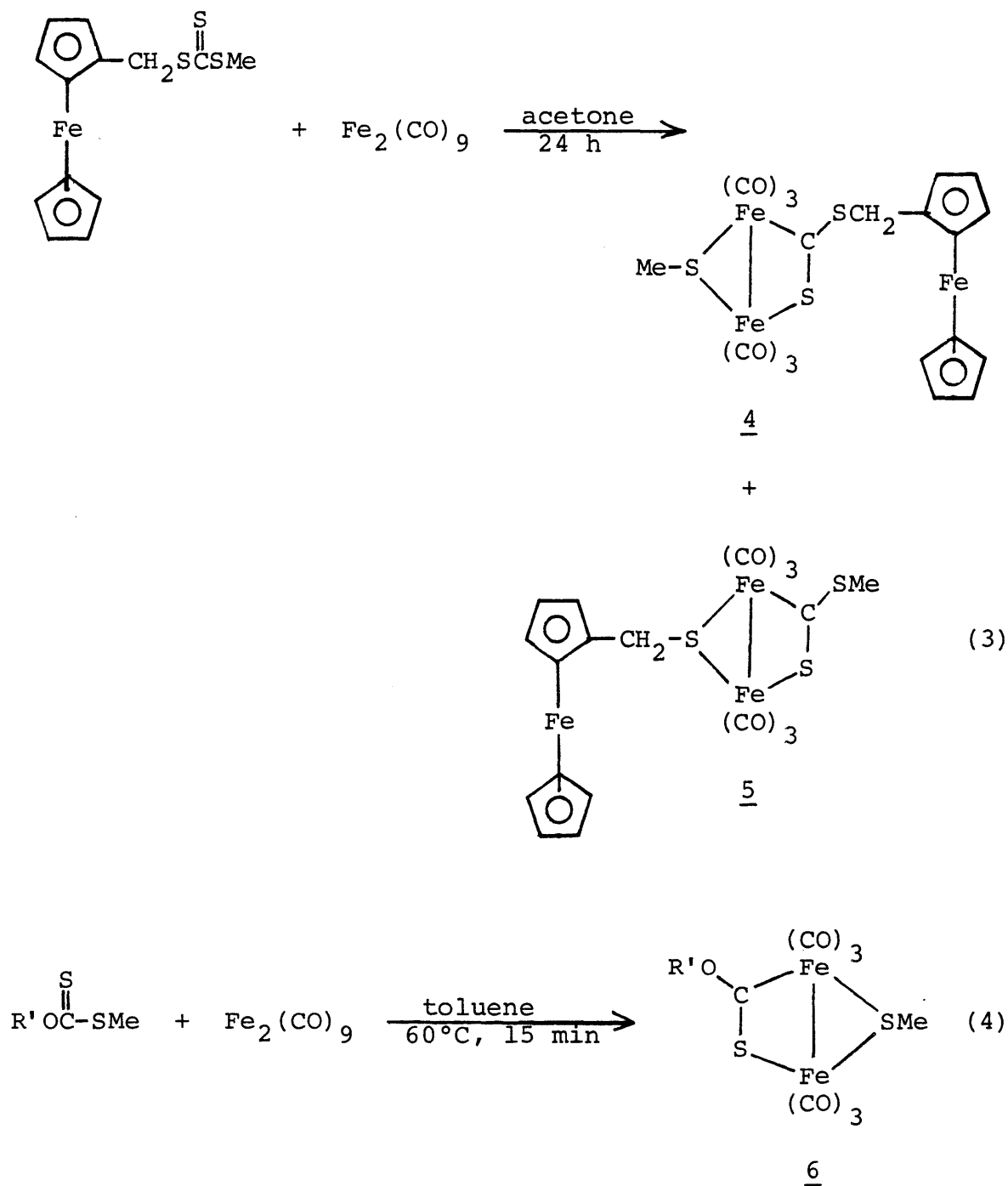
Introduction

Due to the efforts of several research groups the interaction of various organic thiocarbonyl compounds with iron carbonyls has been studied in some detail. Among the thiocarbonyl compounds examined were thioketones,¹ thioesters,^{2,5b} dithioesters,³ thioketenes,⁴ thioamides,⁵ xanthates,⁶ monothiocarbonates,⁷ trithiocarbonates,⁸ dithiochloroformates,^{9a} and N,N-dialkyl thiocarbamoyl chlorides.⁹ Few of these various types of compounds have been systematically or exhaustively studied. However, the reactions which have been reported indicate a strong tendency for the formation of diiron hexacarbonyl complexes often accompanied by the cleavage of carbon-sulfur bonds. In some cases products resulting from complete desulfurization of the organic thiocarbonyl compound have been isolated.^{1c,7}

Among the more studied of the thiocarbonyl compounds are the O-alkyl thiobenzoates² and dithioesters,³ both of which react with $\text{Fe}_2(\text{CO})_9$ to produce similar $\text{Fe}_2(\text{CO})_6$ complexes, (eq.1 and 2). For both types of thioester the thiocarbonyl group readily coordinates, donating four electrons to the $\text{Fe}_2(\text{CO})_6$ system with the other heteroatom datively bound to one of the iron atoms, complexes 1 and 3. In the case of the O-alkyl thiobenzoates (eq.1), the ortho-metallated complexes, 2, also were isolated as minor products. Compounds structurally analogous to 1 and 3 also can be isolated from the reaction of N,N-dialkyl thioamides with $\text{Fe}_2(\text{CO})_9$,⁵ and in one study a trithiocarbonate was found to coordinate in the same manner.¹⁰

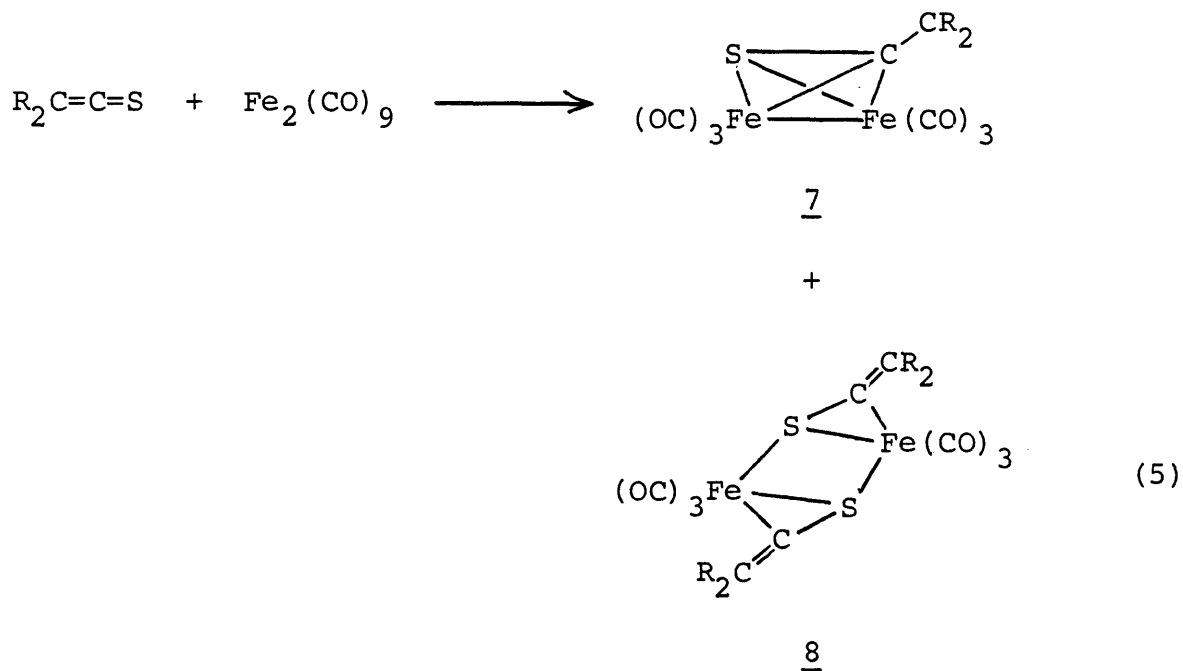


However, going from the thioesters to the trithiocarbonates⁸ and S-alkyl xanthates⁶ generally leads to another type of $\text{Fe}_2(\text{CO})_6$ complex in which a carbon-sulfur bond has been cleaved, (eq.3 and 4). This cleavage results in the formation of a bridging thiolate ligand and coordination of the thiocarbonyl fragment across the two iron atoms as a three-electron donor.



Another example of the tendency of thiocarbonyl compounds to bind two $\text{Fe}_2(\text{CO})_3$ units is found in the report of Behrens et al.⁴ concerning the reaction of thioketenes with diiron

nonacarbonyl, (eq.5). In both products, 7 and 8, the thio

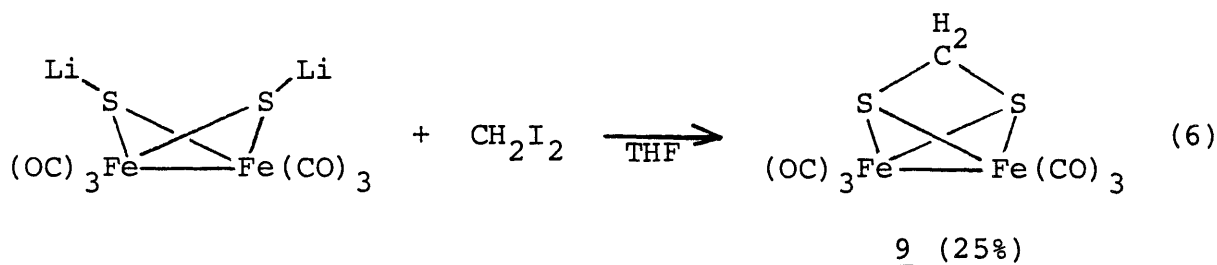


ketene coordinates and bridges the two metals. However, the two complexes differ, 7 has an iron-iron bond with only one coordinated thioketene acting as a six-electron donor, whereas in 8, the two nonbonded iron atoms are held in place with two bridging, four-electron donating thioketene ligands.

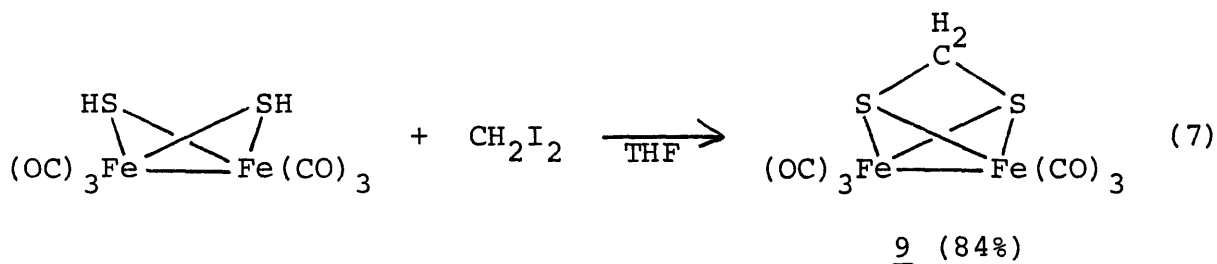
Presented herein are our studies in the area of iron coordinated thiocarbonyl compounds stemming from the modification of prior coordinated organosulfur ligands. From this work compounds structurally analogous to 1, 4, 7 and 8 have been isolated and characterized.

Results and Discussion

During the initial studies of the reactivity of μ -dithio-bis(tricarbonyliron) a synthesis of $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$, 9, was discovered which involved addition of diiodomethane to the $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2-}$ dianion, (eq.6).¹¹ Subsequently it was



found that 9 could be obtained in higher yields by using the Et_3N -induced reaction of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ and diiodomethane, (eq.7).¹² This compound, however, was first reported indepen-



dently by two groups in 1979. Shaver and coworkers obtained 9 as one of the products isolated from the reaction of $\text{Fe}_2(\text{CO})_9$ and 1,3-dithia-5-cycloheptene, (eq.8)¹³ and a Russian group obtained it in very low yield from the reaction of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and diazomethane, (eq.9).¹⁴ Shaver et al.¹³ reported the X-ray structure determination of 9, (Fig.1), but did not

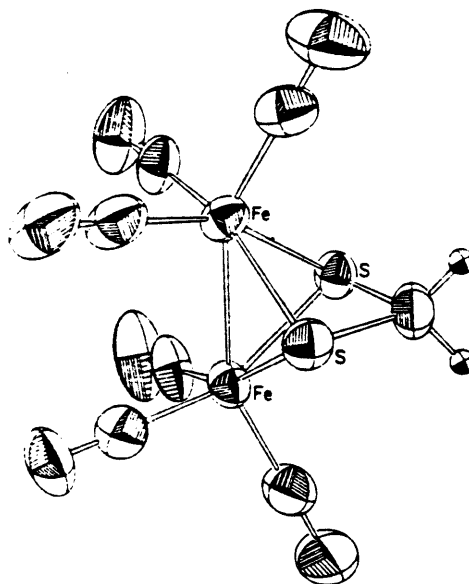
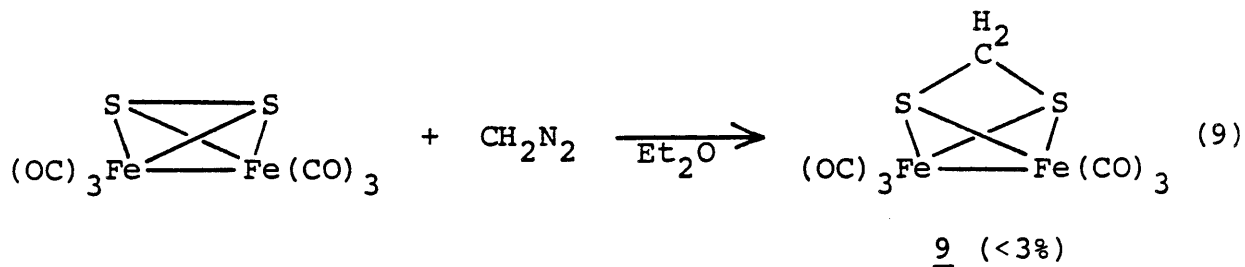
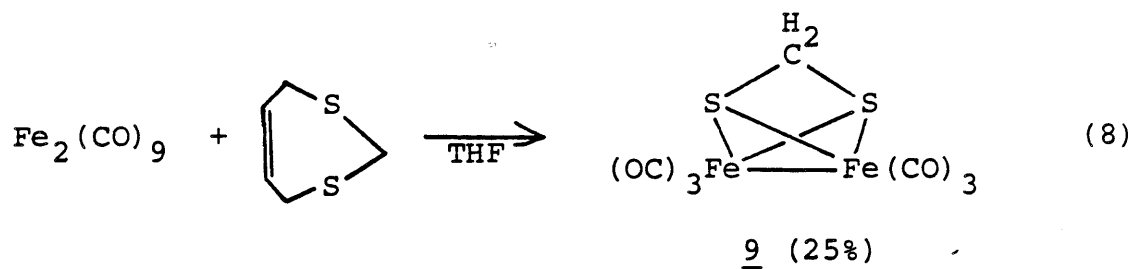
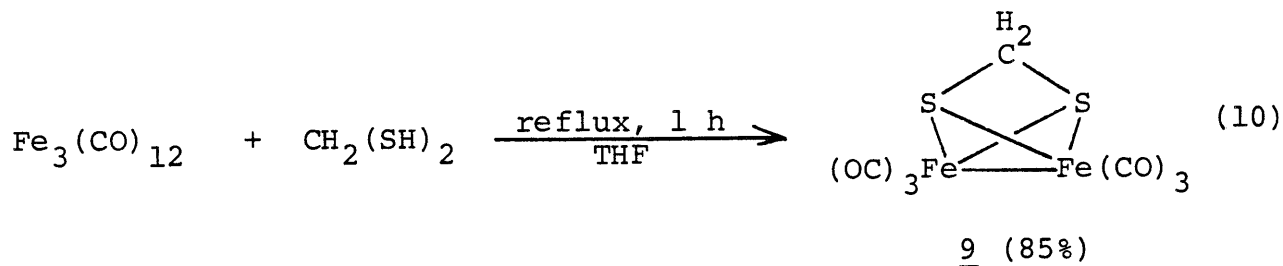


Figure 1. ORTEP drawing of $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$, 9.

investigate any of its chemical properties. Following a report by Huttner¹⁵ that β and γ alkylene dithiols react with $\text{Fe}_3(\text{CO})_{12}$ to give good yields of alkylene-bridged

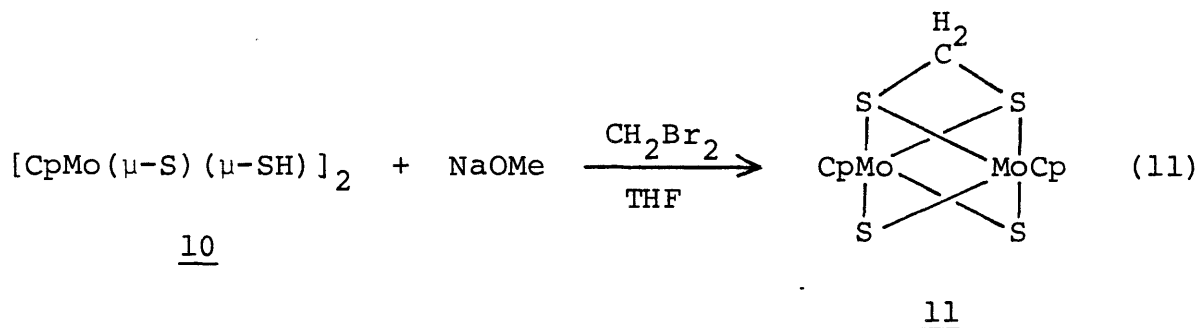
derivatives of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, the latest synthesis of 9 was developed in these laboratories. Thus, it was found that methanedithiol would react with $\text{Fe}_3(\text{CO})_{12}$ in THF at reflux for 1 h to yield 9 in 85% yield (eq.10). Compound 9 is a dark



red, crystalline material, mp 73-75°C; the methylene protons appear as a singlet at δ 4.61 in the ^1H NMR spectrum and the ^{13}C NMR spectrum¹³ shows a triplet at δ_{C} 62.35 ($J = 185\text{Hz}$) for the methylene carbon and a singlet at δ_{C} 209.3 for the carbonyl ligands.

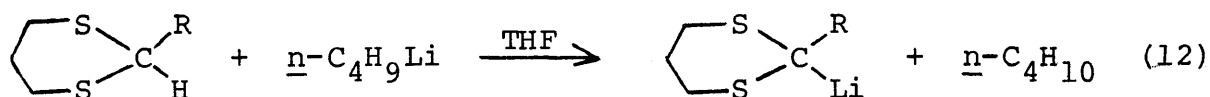
The methanedithiolate unit as a ligand in transition metal chemistry has not aroused a great deal of interest among inorganic chemists. In 1979, the year that the first reports concerning the synthesis and structure of 9 appeared, two other groups reported the isolation of complexes containing the methanedithiolate ligand. For one complex, however, the bis-(tetraphenylphosphonium) salt of $[\text{W}_3\text{S}_8(\text{S}_2\text{CH}_2)]^{2-}$, no spectroscopic data was supplied.¹⁶ It was isolated from the reaction mixture obtained by placing $(\text{Ph}_4\text{P})_2(\text{WS}_4)$ in a refluxing $\text{CH}_2\text{-Cl}_2$ /acetone solution. Adams and Golembeski reported the other example, which contains a methanedithiolate ligand bound to two $[\text{HOs}_3(\text{CO})_{10}]$ clusters, produced when $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was placed

in refluxing carbon disulfide.¹⁷ In 1983, Rakowski DuBois reported the preparation of 11 by the deprotonation of the corresponding dithiol complex, 10, in the presence of methylene bromide, (eq.11).¹⁸ Subsequently, 11 has been the precursor



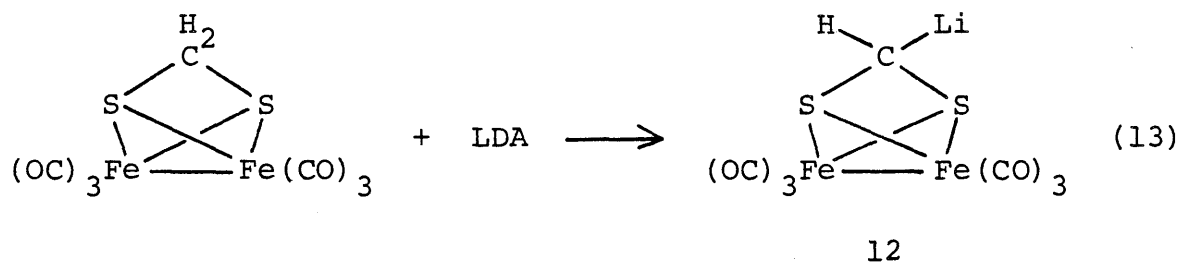
to a number of derivatives produced by the linkage of olefins and acetylenes between the two sulfido ligands. Single crystal X-ray diffraction studies have been reported for one such derivative and another with methyl groups on the bridging sulfido units.^{18b}

A notable feature of $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$ is that it has a methylene group flanked by two sulfur atoms. Such a structural feature in organosulfur compounds is known to increase the acidity of the methylene protons.¹⁹ This is demonstrated by the facile metallation of 1,3-dithianes with strong organic bases, (eq.12).¹⁹ Based on this precedent, the deprotonation



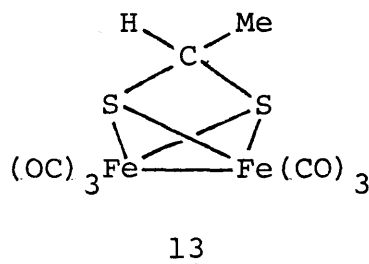
of 9 to generate the organolithium reagent, 12, appeared to

be a reasonable reaction to attempt, (eq.13). It was expected



also that the metalation might be made even more favorable by lone-pair donation of the sulfur atoms to iron which would result in a partial positive charge on the sulfurs. If the generation of 12 could be accomplished, it would provide a route to mono- and possibly disubstituted derivatives of 9.

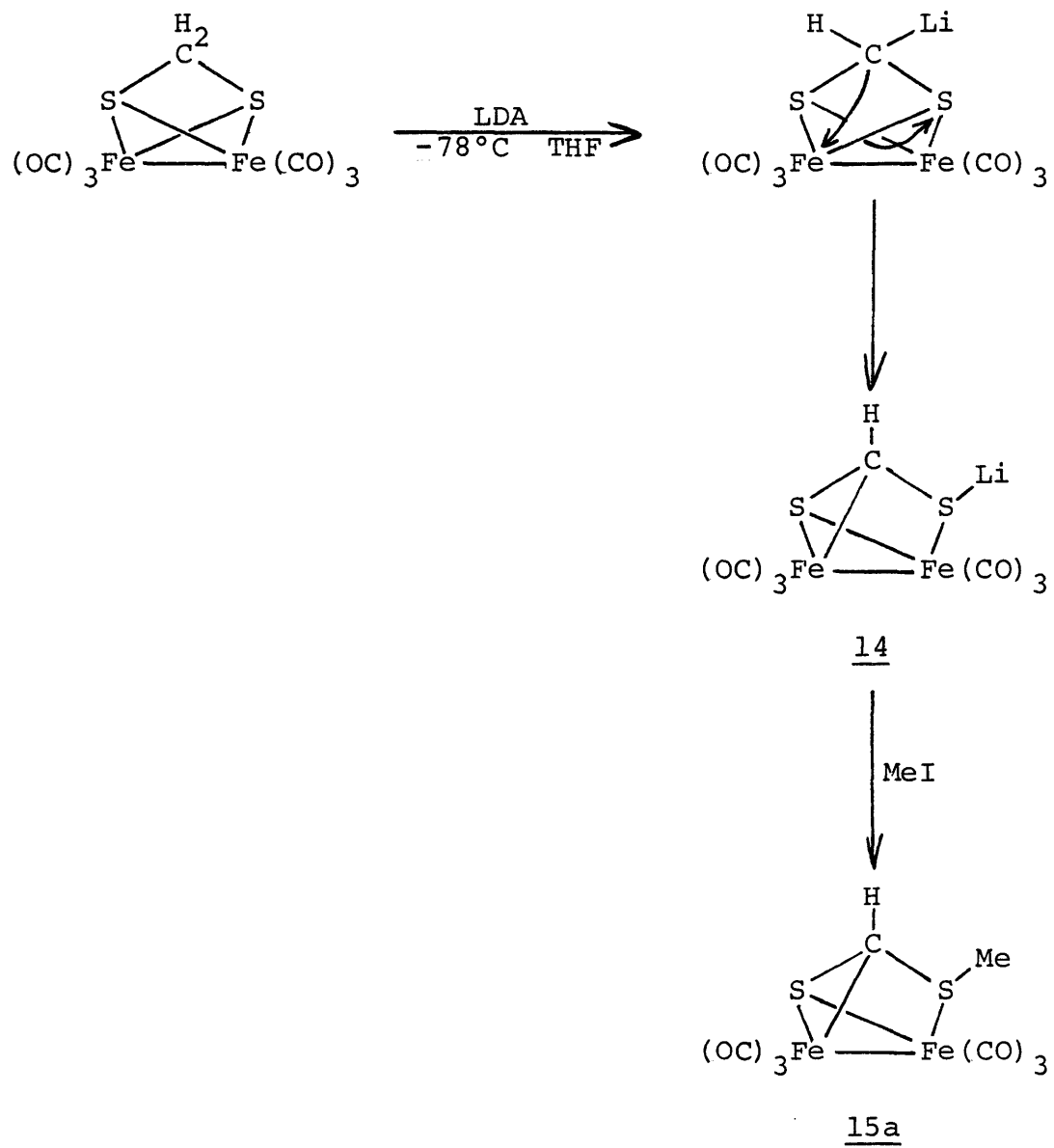
The addition of a slight excess of LDA (lithium diisopropylamide) to 9 in THF at -78°C resulted in a dramatic color change from red to green. To this reagent solution was added iodomethane and as the mixture was allowed to warm to room temperature it became red. Removal of the solvent followed by filtration chromatography (silicic acid; elution first with pentane, then with 1/9 CH_2Cl_2 /pentane) gave a 78% yield of a dark red oil. The mass spectrum and combustion analysis indicated the oil to have the elemental composition of 13 which



was the expected product. However, the ^1H NMR spectrum (CDCl_3 , 90MHz) revealed no spin-spin coupling between the methine and the methyl protons as would be anticipated for 3. Instead the spectrum consisted of two singlets at δ 3.89 (1H) and 2.33 (3H). The proton-coupled ^{13}C NMR spectrum (CDCl_3 , 22.5MHz) confirmed the presence of the methyl and methine carbons; δ_{C} 35.4 (q, $J = 141\text{Hz}$, CH_3) and 55.4 (d, $J = 188\text{Hz}$, CH).

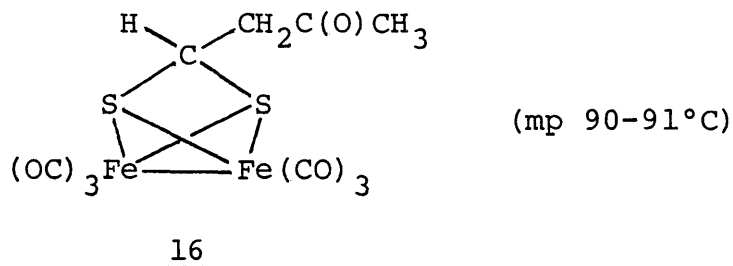
Based on this information, the product of this reaction did not seem to be 13, but did appear to be an isomer of 13. Therefore, structural alternatives had to be considered. The observed green color of the deprotonated intermediate in this reaction suggested that sulfur-centered anions might be involved, since this is the characteristic color of sulfur-centered anions derived from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$.^{11,20,21} Scheme 1, therefore, depicts a reaction course which would involve just such intermediates and provide an isomeric alternative to 13. Basically the proposed mechanism suggests the occurrence of an intramolecular nucleophilic substitution reaction at iron with the displacement of sulfide ion by the carbanion. Interception of 14 by iodomethane would lead to the isolation of 15a, a compound for which no spin-spin coupling would be observed between the methine and methyl protons. Structurally, 15a has precedent in the chemical literature, (eq.1 and 2).^{2,3,5} Patin et al.³, who reported that dithioesters and $\text{Fe}_2(\text{CO})_9$ would react to form compounds of type 2, confirmed the structure of these complexes with an X-ray diffraction study for $\text{R} = \text{---}\text{C}_4\text{H}_3\text{S}$. Thus to consider a rearrangement as depicted in Scheme 1 to give

Scheme 1

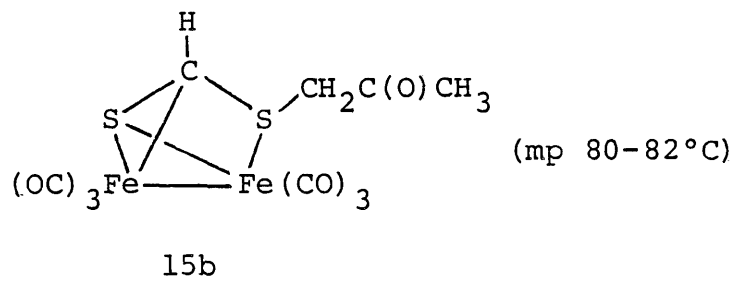


products structurally analogous to 2 was not unreasonable.

Since 15a was a red oil, the use of X-ray crystallography was not possible to confirm its structure. So other means were sought. In previous research a synthesis of 16 had been



accomplished by the piperidine-induced addition of $(\mu\text{-HS})_2\text{Fe}_2(\text{CO})_6$ to $\text{HC}\equiv\text{CC}(\text{O})\text{CH}_3$.²² This red solid compound did display spin-spin coupling between the methine and methylene protons in its ^1H NMR spectrum (CDCl_3); δ 2.10 (s, 3H, CH_3), 3.08 (d, $J = 6.5\text{Hz}$, 2H, CH_2) and 5.02 (t, $J = 6.5\text{Hz}$, 1H, CH). Since 16 was available for direct comparison, bromoacetone was used to quench the $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6/\text{LDA}$ reaction mixture (0.5 h at -78°C then 2.5 h at room temperature). Isolation of a red solid, mp $80\text{-}82^\circ\text{C}$, was accomplished in 55% yield. This new compound, 15b, was obviously not 16, but by its mass spectrum



and combustion analysis did have the same elemental composition. Again the methine proton appeared as a singlet, δ 3.94, in the ^1H NMR spectrum and the methylene group as an AX quartet, δ 3.50 and 3.69 ($J_{\text{AX}} = 13.9\text{Hz}$). The diastereotopic nature of the methylene protons in 15b is reasonable since the carbon bound to iron is chiral. This same observation was also made for the type 3 complexes.³ The spectral data and comparison of 15b and 16 left no doubt that alkylation of the $(\mu\text{-CH}_2\text{S}_2)\text{-Fe}_2(\text{CO})_6$ intermediate was not occurring at carbon and strongly supported quenching at sulfur after an intramolecular rearrangement of the initially formed carbanion intermediate, Scheme 1.

With both 15b and 16 being crystalline solids, an X-ray diffraction study of each, was performed in collaboration with Dr. M. Cowie and Dr. B.W. Hames, to completely settle the structural question. Figure 2 presents the structure of 16 confirming the presence of a gem-dithiolate ligand, which would have been expected in 15b had alkylation occurred at carbon in the $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6/\text{LDA}$ anionic intermediate. The salient features of 16 have already been discussed in Chap.2 . The X-ray structure determination of 15b, Figure 3, confirmed that it had the structure proposed on the basis of the spectroscopic data. Thus only S(1) is bound to both iron atoms; S(2), being datively bonded only to Fe(2), has been displaced from Fe(1) by the formation of the Fe(1)-C(7) bond in the anionic intermediate. The quenching electrophile thus reacted at S(2) to which the $\text{CH}_2\text{C}(\text{O})\text{CH}_3$ group is bound. The rearrangement

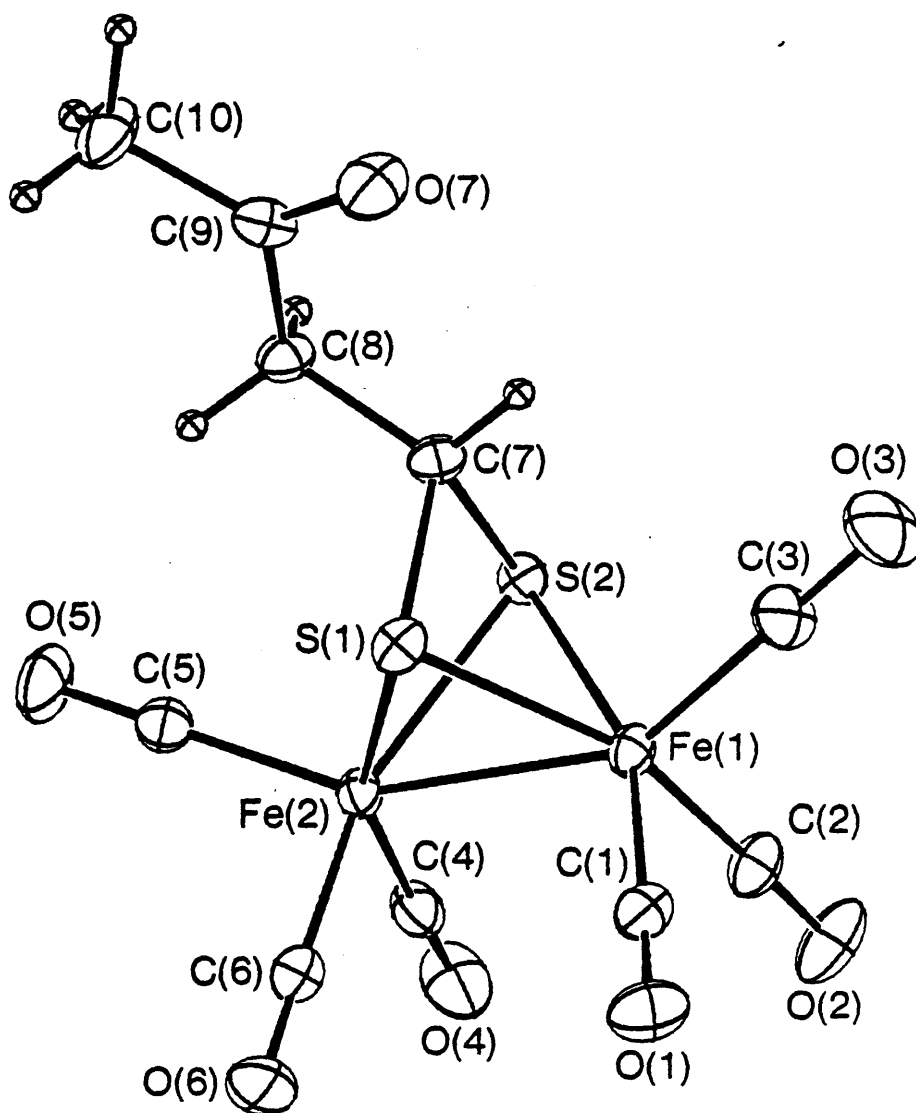


Figure 2. Perspective drawing of $(\mu\text{-CH}_3\text{C(O)CH}_2\text{CHS}_2)\text{Fe}_2(\text{CO})_6$, 16.

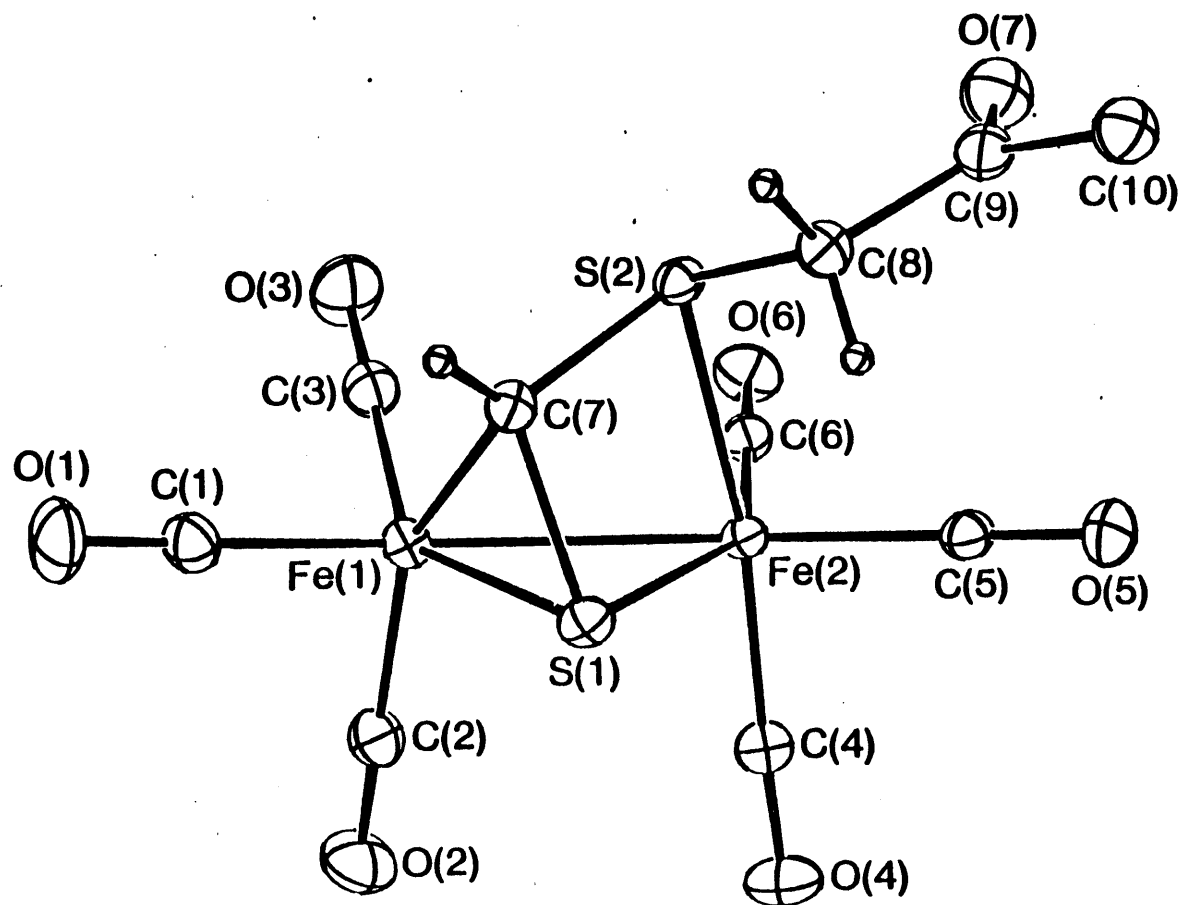


Figure 3. Perspective drawing of $(\mu\text{-CH}_3\text{C(O)CH}_2\text{SCHS})\text{Fe}_2(\text{CO})_6$, 15b. Thermal ellipsoids are drawn at the 20% probability level except for hydrogens which are drawn artificially small.

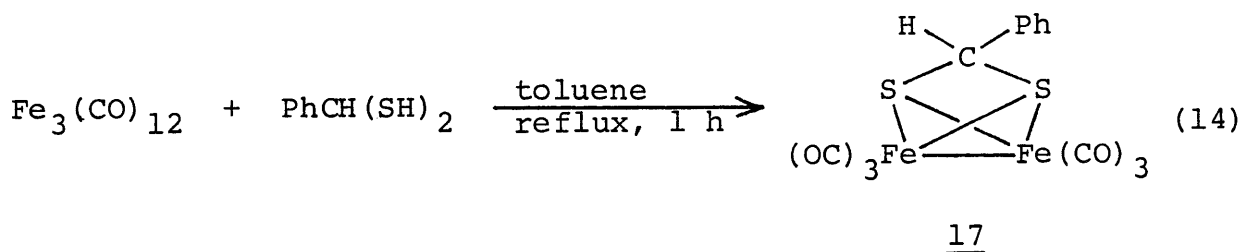
Table 1. Some Relevant Bond Lengths ($\overset{\circ}{\text{\AA}}$) and Angles (deg) for
Compound 15a.

<u>(i) Bond Lengths</u>	<u>(ii) Bond Lengths</u>
Fe(1)-Fe(2) 2.6273(10)	S(1)-Fe(1)-C(7) 49.7(1)
Fe(1)-S(1) 2.1925(14)	S(1)-Fe(1)-Fe(2) 55.69(4)
Fe(1)-C(7) 1.998(4)	C(7)-Fe(1)-Fe(2) 69.6(1)
Fe(2)-S(1) 2.2838(14)	C(7)-S(1)-Fe(1) 59.4(1)
Fe(2)-S(2) 2.3042(13)	C(7)-S(1)-Fe(2) 82.0(2)
S(1)-C(7) 1.771(5)	Fe(1)-S(1)-Fe(2) 71.85(4)
C(7)-S(2) 1.775(5)	S(2)-Fe(2)-S(1) 77.26(5)
S(2)-C(8) 1.831(4)	S(2)-Fe(2)-Fe(1) 76.10(4)
C(8)-C(9) 1.520(7)	S(1)-Fe(2)-Fe(1) 52.46(4)
C(9)-C(10) 1.517(7)	C(7)-S(2)-Fe(2) 81.4(2)
C(9)-O(7) 1.217(7)	C(7)-S(2)-C(8) 103.0(2)
C(7)-H(71) 0.98(4)	C(8)-S(2)-Fe(2) 109.2(2)
	S(1)-C(7)-Fe(1) 70.9(2)
	S(2)-C(7)-Fe(1) 107.8(2)
	S(1)-C(7)-S(2) 107.8(2)

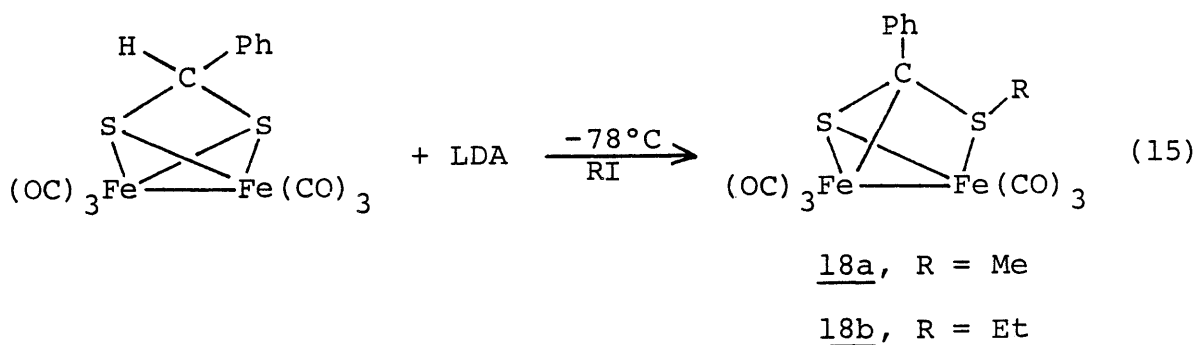
has caused the loss of the "butterfly" geometry of the starting material, but the new ligand is still an overall six-electron donor. The C(7)-S(1) moiety can be viewed as a thiocarbonyl unit side-on bonded to Fe(1). The C(7)-S(1) and C(7)-S(2) bonds (1.771(5) and 1.775(5) Å, respectively) are both shorter than normal C-S single bonds, in contrast to the S(2)-C(8) length of 1.831(4) Å, suggesting some multiple-bond character. The structure of 15b thus confirms that a rearrangement of the initially formed organolithium reagent must be occurring which can reasonably be depicted by Scheme 1.

Other alkyl derivatives were made in a similar fashion. The ethyl derivative, a dark red oil, was isolated in 68% yield. Its ^1H NMR spectrum showed a complex multiplet for the methylene protons instead of a quartet due to the chirality of the complex. The benzyl and allyl derivatives also were made in 56 and 70% yield, respectively. All of these compounds showed a singlet in their ^1H NMR spectra assignable to the methine proton, confirming that they all had the same structure as 15b.

$(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$ proved not to be the only alkylene bridged derivative of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ capable of being deprotonated. Another gem-dithiolate- $\text{Fe}_2(\text{CO})_6$ complex 17, mp 92-94°C, was prepared in 22% yield from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and α,α -toluenedithiol²³ in refluxing THF, (eq.14).²⁴ The methine proton of 17 was expected to be just as acidic as the methylene protons of 9. However, deprotonation of 17 will initially form a benzyl anion, so it was wondered whether this



added resonance stabilization of the organolithium reagent would hinder its tendency to rearrange to a sulfur-centered anion. When a slight excess of LDA (9.0 mmol) was added to a red THF solution of 17 (0.83 mmol) at -78°C an immediate color change to emerald green was observed, indicative of an anionic rearrangement. Addition of an excess of iodomethane to the solution which then was allowed to warm to room temperature caused a color change to red. Removal of the solvent and filtration chromatography of the residue resulted in the isolation of 18a in 78% yield, mp $101-102^\circ\text{C}$, (eq.15). The



ethyl derivative, a red oil, 18b, was made in a manner like that from iodoethane in 61% yield. The proton NMR spectrum (90MHz, CD_2Cl_2) of 18b showed the SCH_2 protons as a complex multiplet (δ 2.53) resulting from the chirality of the compound

which renders them diastereotopic. Further proof that alkylation has occurred at sulfur is provided by the six line pattern in the terminal carbonyl region of their IR spectra (in pentane) similar to the pattern observed for the type 15 complexes, Figure 4. The ^{13}C NMR spectra of 18a and 18b showed the iron-bound carbon at δ_{C} 73.7 and 72.4, respectively, being slightly more shielded than the bridging carbon of the starting material, 17. The same trend was observed for the dithio carbon in the rearrangement products derived from 9, Table 2. In the carbonyl region of the ^{13}C NMR spectra for compounds 15 two signals were always observed, one sharp, the other broad. This is the result of two independently fluxional $\text{Fe}(\text{CO})_3$ units between which there is no scrambling of CO ligands.¹⁰ The two fluxional processes apparently occur at different rates, the slower resulting in a broad signal at room temperature. This same behavior was noted for 18b, Table 2, although for 18a only one broad signal was observed presumably due to an overlap of the two expected signals. Although 18a has been reported previously, being isolated from the reaction of methyl dithiobenzoate and $\text{Fe}_2(\text{CO})_9$, no spectroscopic data were supplied with which a comparison could be made.³

Thus the phenyl group had no effect on the ability of the initially formed carbanion derived from 17 to displace a sulfur atom at iron.

Extending these studies to other alkylene bridged derivatives of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, Gallagher found that the same intramolecular substitution reaction would occur when 19 and 20 are

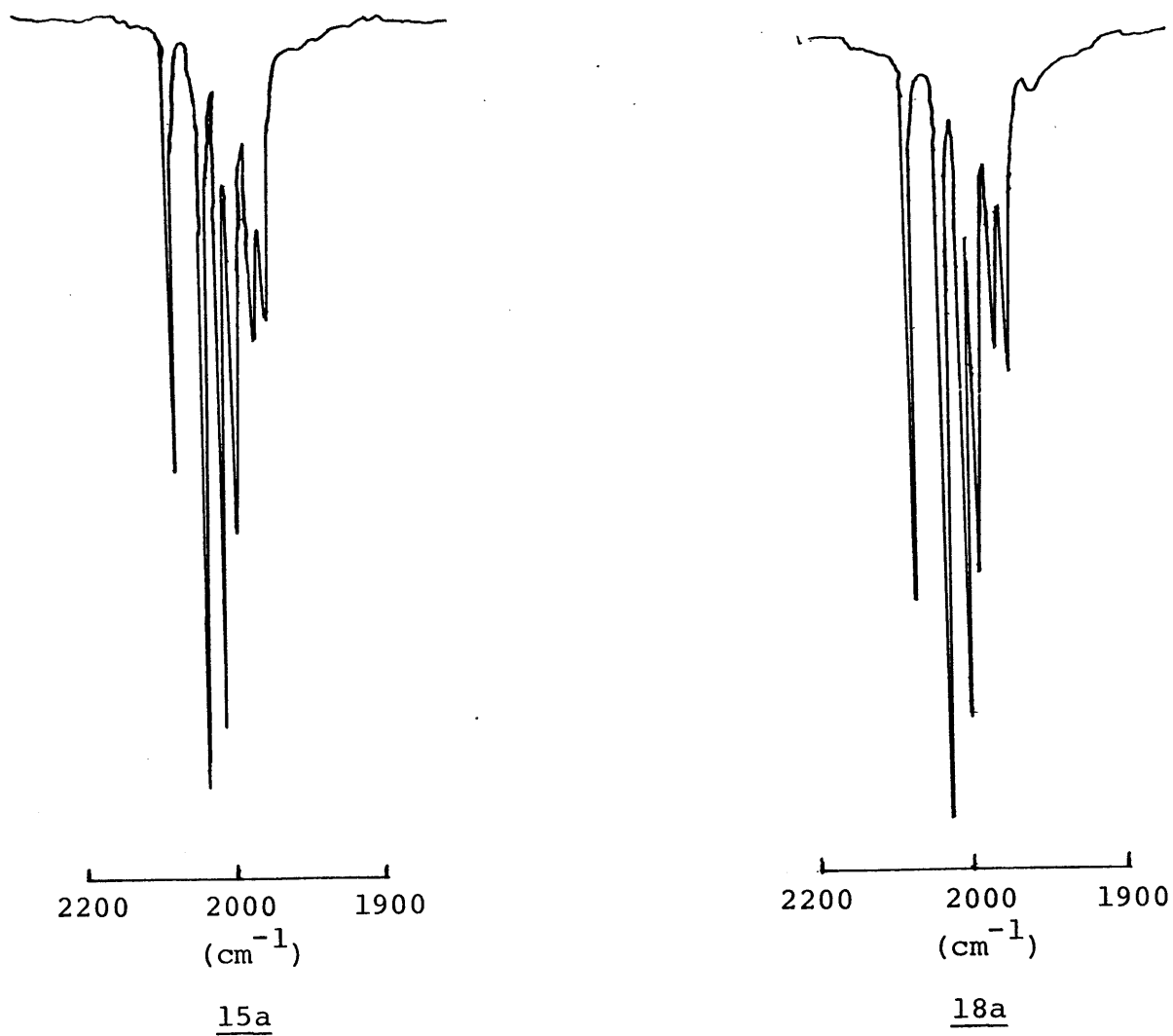
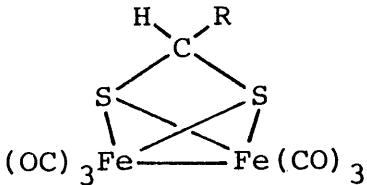
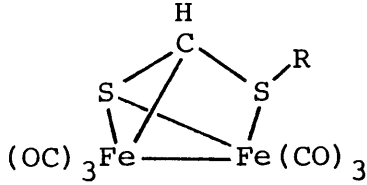
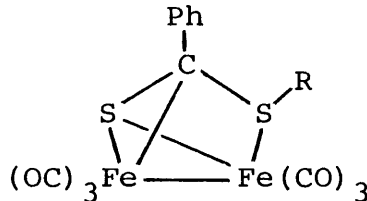
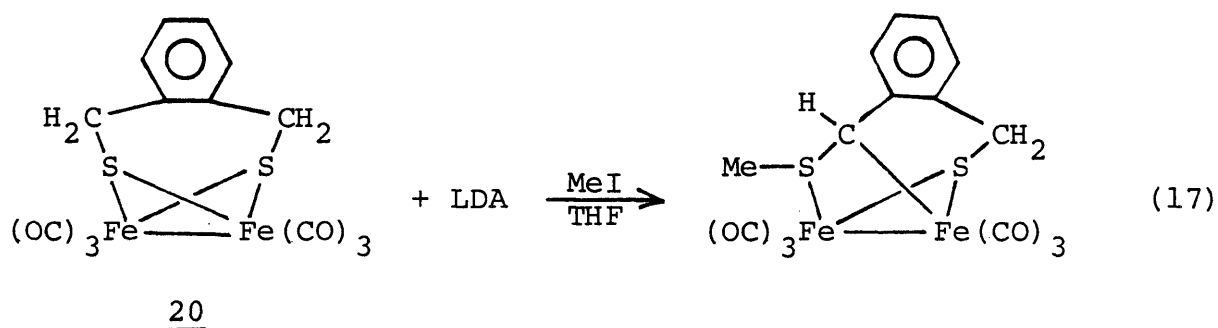
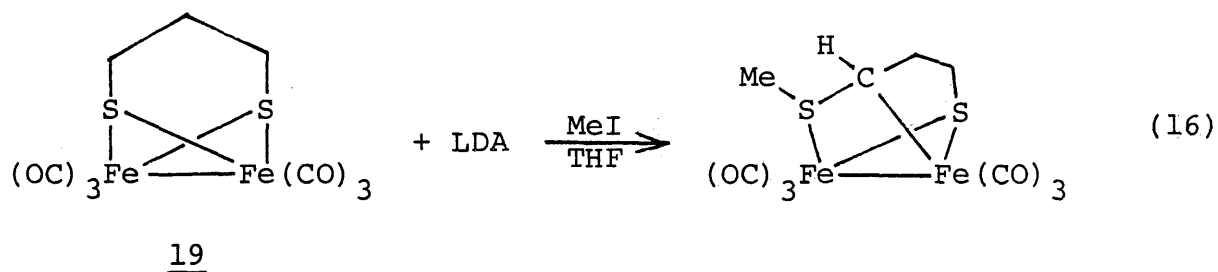


Figure 4. Comparison of the terminal carbonyl region of the IR spectra 15a and 18a in pentane.

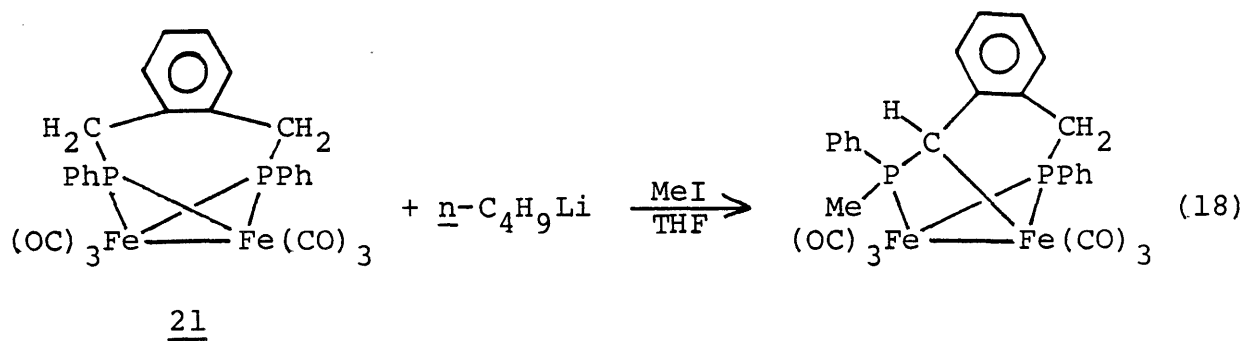
Table 2. ^{13}C NMR Data for gem-Dithiolate and Dithioester- $\text{Fe}_2(\text{CO})_6$ Complexes.

	R	$\delta_{\text{C S}_2\text{C}}$	$\delta_{\text{C Fe-CO}}$
	H^{13}	62.35 (t, $J = 158\text{Hz}$)	209.3
	Ph	79.1 (d, $J = 166\text{Hz}$)	208.0, 208.4
	Me	55.4 (d, $J = 188\text{Hz}$)	208.0(br), 211.2
	Et	52.2 (d, $J = 188\text{Hz}$)	208.8(br), 211.3
	CH_2Ph	52.4 (d, $J = 192\text{Hz}$)	208.6(br), 211.1
	allyl	52.0 (d, $J = 187\text{Hz}$)	208.5(br), 211.2
	$\text{CH}_2\text{C}(\text{O})\text{CH}_3$	53.4 (d, $J = 190\text{Hz}$)	208.3(br), 210.9
	Me	73.7	211.6(br)
	Et	72.4	209.7(br), 211.6

treated with LDA in THF at -78°C , (eq.16 and 17).²⁵ When the



phosphido analog of 20, 21, was treated with n-butyllithium at -78°C , Wood found that a methylene proton could be removed.²⁶ The resulting carbanion, stable at -78°C , attacked an iron atom with concomitant Fe-P bond heterolysis when warmed to -20°C , (eq.18).

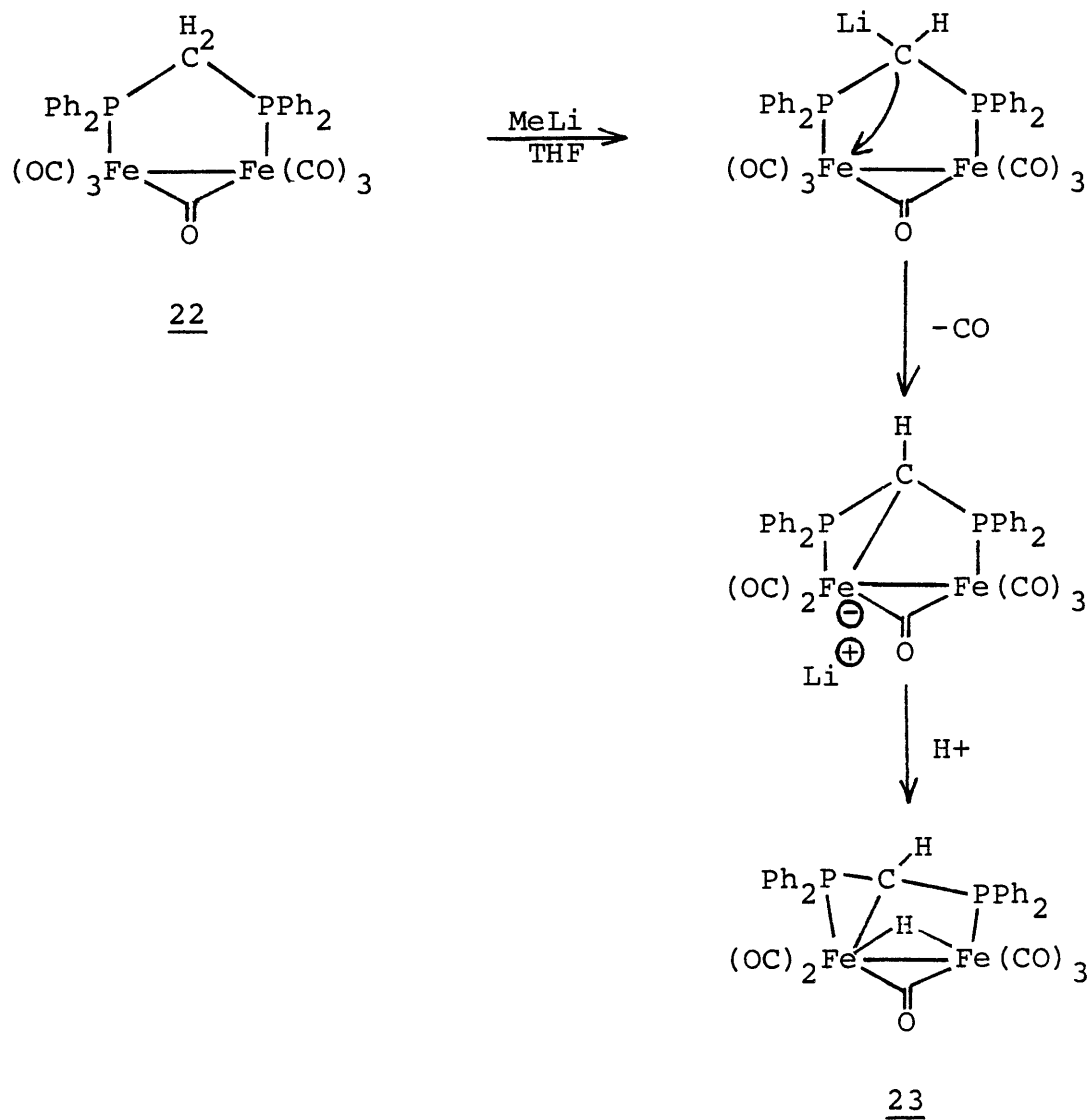


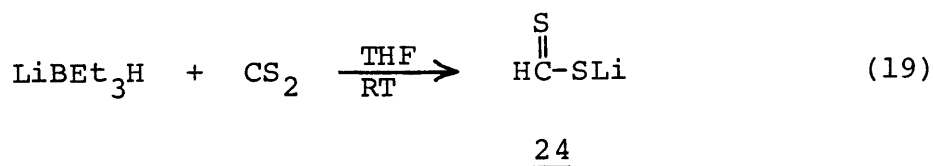
Formation of metallacycles of the type $\overline{\text{MCH}_2\text{PMe}_2}$ have also been recently obtained after deprotonation of the PMe_3 ligand and concomitant nucleophilic attack of the carbanion at the metal.^{27,28} In a somewhat similar system to 9, Stone et al. have reported the deprotonation of the methylene unit in 22 with methyllithium, Scheme 2.²⁹ Nucleophilic attack of the carbanion at iron led to the displacement of a carbonyl ligand which, followed by protonation, allowed isolation of the bicyclic compound 23.

As already discussed, the overall structure of 15b is the same as that found by Patin and co-workers for dithioester - $\text{Fe}_2(\text{CO})_6$ complexes, synthesized as outlined in eq.2 . This similarity leads to the conclusion that complexes of type 15 can be regarded as diiron hexacarbonyl-coordinated alkyl dithioformates. This being the case, it was of interest to see if these compounds were more readily accessible by the direct reaction of alkyl dithioformates and iron carbonyls. Alkyl dithioformates, however, are not readily available as starting materials. When their synthesis is attempted they trimerize to give heterocycles with the trithiane structure.^{30,31} Therefore a simple in-situ method of preparing dithioformate esters, which then could be reacted with $\text{Fe}_2(\text{CO})_9$ before trimerization, was needed.

With this goal in mind, it has been found that LiBEt_3H (super-hydride, Aldrich) will react with CS_2 to form orange THF solutions of lithium dithioformate, (eq.19). When such an orange solution was cannulated into a THF solution of

Scheme 2



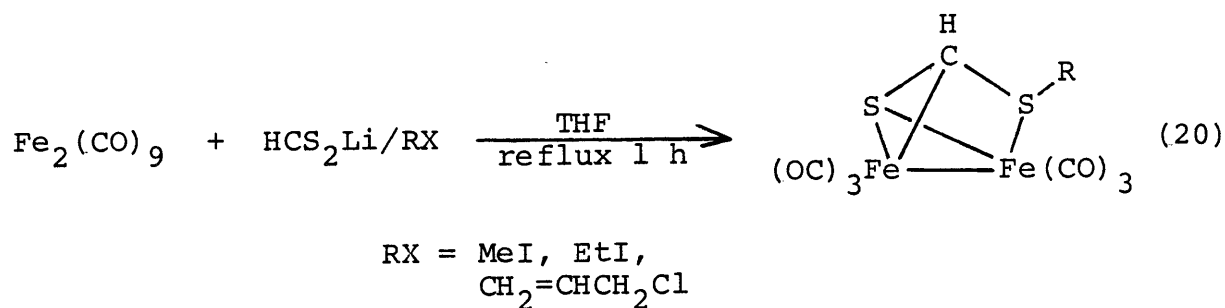


$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ the ensuing reaction (20 h) produced $\eta^5\text{-C}_5\text{H}_5\text{-Fe}(\text{CO})_2\text{SC}(\text{S})\text{H}$, 25, in 77% yield. This η^1 -dithioformate derivative was isolated as an air-stable, red-brown solid, mp 61-63°C, the ^1H NMR spectrum of which revealed two singlets at δ 5.08 (5H) and 11.27 (1H). In the ^{13}C NMR spectrum, the dithioformate carbon appears as a doublet at δ_{C} 233.1 ($J = 174\text{Hz}$). The presence of two bands for terminal carbonyls at 2051 and 2010 cm^{-1} in the IR spectrum and the parent ion in the mass spectrum confirmed the η^1 bonding mode of the HCS_2 ligand. The oxo analog of 25 has been reported and the structure determination appeared recently.³²

The synthesis of 25 served to prove that the dithioformate anion could be produced from the reaction of LiBEt_3H and CS_2 as a useful intermediate. In a standard procedure, a THF solution of LiBEt_3H was added dropwise at room temperature to a THF solution of carbon disulfide. The reaction was instantaneous and exothermic, producing a light orange mixture containing HCS_2Li . The dithioformate anion has been generated previous to this work by the reaction of HCCl_3 with K_2S ³³ and by the action of NaBH_4 on CS_2 in the presence of amines.³⁴ Although the reactivity of potassium dithioformate toward some metal and alkyl halides was studied,³³ it was not until recently that a report appeared on the reaction of the dithioformate

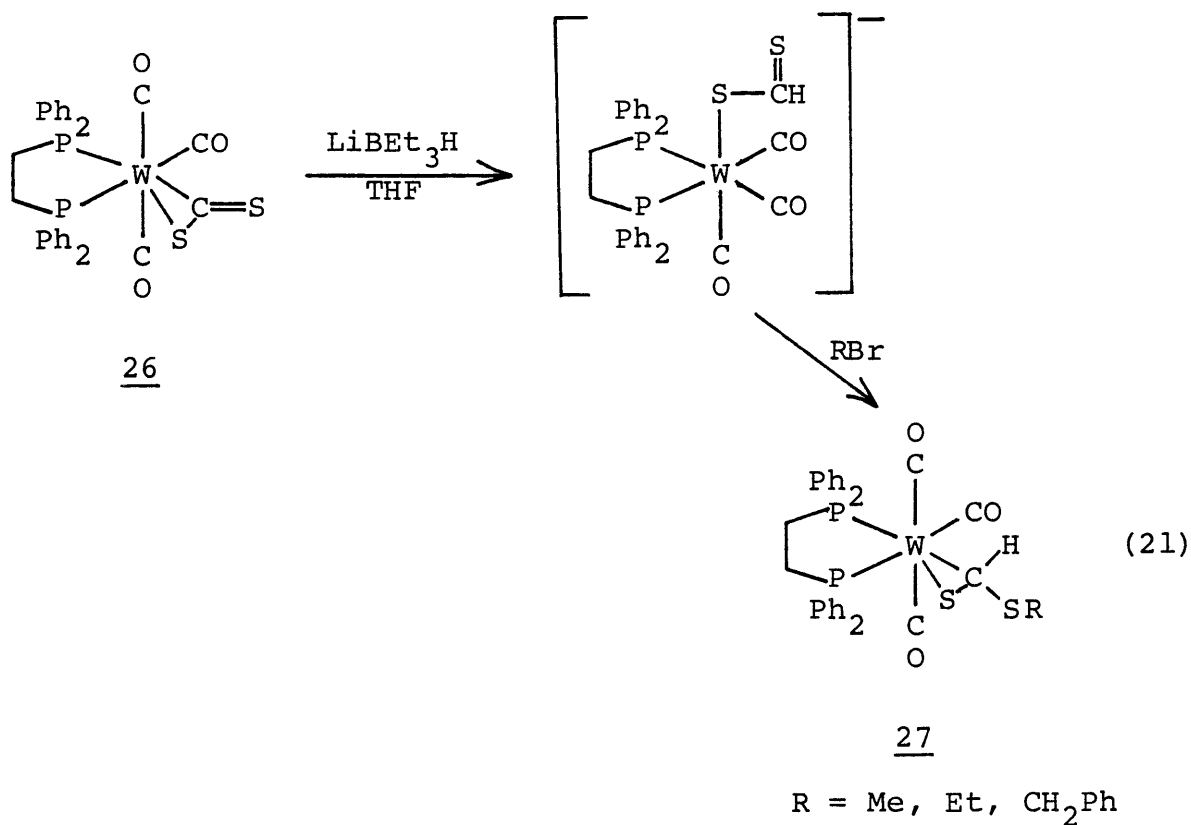
anion with a transition metal complex.³⁵

This new method of generating the dithioformate anion was next tested as a step in the synthesis of complexes of type 15. Thus an excess of iodomethane was added to a HCS_2Li THF solution which was then cannulated into an $\text{Fe}_2(\text{CO})_9/\text{THF}$ mixture and refluxed for 1 h. Removal of the solvent followed by filtration chromatography (silicic acid; eluting with 9/1, v/v pentane/ CH_2Cl_2) led to the isolation of 15a in 30% yield, based on CS_2 , (eq.20). Using the same procedure, the ethyl and allyl

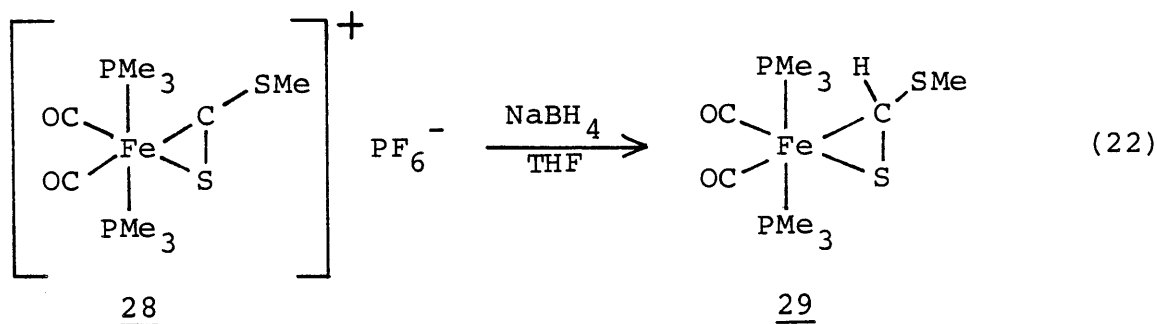


derivatives were produced in 30 and 12% yields, respectively, from ethyl iodide and allyl chloride. This reaction thus provides a convenient, direct route to these compounds from simple, readily available starting materials.

Synthesis of the type 15 complexes via the deprotonation of 9 provided the first reported examples of coordinated dithioformic acid esters.³⁶ Two subsequent reports of these ligands have recently appeared. Schenk and Schwietzke found that with a synthetic strategy reminiscent of eq.19 LiBEt_3H could be used to add to hydride to the CS_2 ligand of 26, (eq. 21).³⁵ Alkylation of the resulting dithioformate ligand with

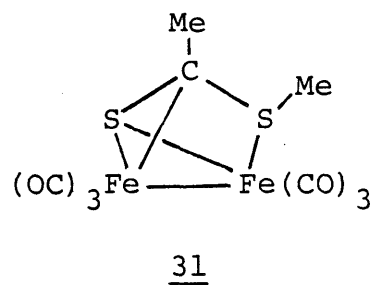
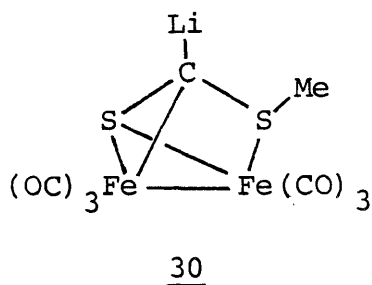


one equivalent of an alkyl bromide provided the compounds 27. In a similar study it was reported that NaBH_4 would react with the cationic species 28 in THF to afford the new methyl dithioformate complex 29 in 51% yield, (eq.22).³⁷ Both of these



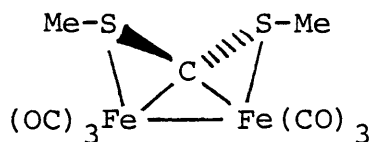
complexes, 27 and 29, are mononuclear with $\eta^2\text{-HCS}_2\text{R}$ ligands acting as two- electron donors in contrast to compounds 15 where the HCS_2R ligand is a bridging six-electron donor.

Since the type 15 compounds contain a C-H moiety in which the carbon atom is flanked by two sulfur atoms (C(7), Figure 3), it was postulated that this hydrogen atom also could be acidic enough to be removed with LDA. Following the same procedure used to deprotonate 9, 15a (1.68 mmol) was dissolved under nitrogen in THF and cooled to -78°C , whereupon, a slight excess of freshly prepared LDA (1.90 mmol) was added. The 15a solution darkened to a red-brown and was stirred for 45 min. Upon addition of an excess of iodomethane, the solution was removed from the cold bath was stirred for 22 h. Removal of the solvent and column chromatography of the remaining residue (silicic acid; 1/1, v/v pentane/ CH_2Cl_2) resulted in the isolation of an orange solid, mp 130°C dec, in 77% yield. The mass spectrum and combustion analysis of this new compound confirmed a molecular formula of $(\text{CH}_3)_2\text{CS}_2\text{Fe}_2(\text{CO})_6$, proving that deprotonation had occurred and that a methyl group had been incorporated into the product. The question remaining was whether an intramolecular rearrangement of the type depicted in Scheme 1 had occurred. If a carbanion intermediate, 30, had been methylated, the product 31, a dithioester complex,

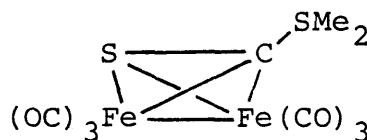


would have been formed. This compound, however, was ruled out on the basis of spectroscopic data. The ^1H NMR spectrum (CDCl_3 , 90MHz) showed a singlet at δ 2.80; 31 would be expected to have two singlets for inequivalent methyl groups. Patin has reported that complexes of type 31 have characteristic chemical shifts of approximately δ_{C} 85 for the dithio carbon in their ^{13}C NMR spectra.³ As already observed for 18a and 18b, the dithio carbon appeared at δ_{C} 73.7 and 72.4, respectively. However, the ^{13}C NMR spectrum of the product derived from the deprotonation of 15a showed no signals in this region but did have a singlet at δ 106.7 as well as a quartet, δ 3.22 ($J = 144\text{Hz}$), for the methyl groups and a singlet, δ 214.0, for the carbonyl carbons. These data led to the conclusion that a rearrangement of the initially formed organolithium reagent, 30, had occurred.

Consideration of the structure of 15a reveals that there are two Fe-S bonds which could be cleaved by nucleophilic attack of the carbanion at iron to yield products, 32 and 33,



32



33a

consistent with the spectral data. Compound 32 represents a bridging dithiocarbene complex in which the thiomethyl groups are datively bound to the iron atoms. With a tetrahedral

carbene carbon, the two methyl groups would be expected to appear equivalent in the ^1H NMR spectrum. The isomeric alternative, 33a, would also be expected to harmonize with the spectroscopic data. The mass spectrum, however, showed peaks resulting from the loss of Me_2S at 212 ($\text{M}^+ - 4\text{CO} - \text{Me}_2\text{S}$), 184 ($\text{M}^+ - 5\text{CO} - \text{Me}_2\text{S}$), 156 (Fe_2SC) and 62 (Me_2S) which, although suggesting the molecule contained a Me_2S group, could not be taken as absolute confirmation that the product was 33a.

In need of conclusive structural data, an X-ray diffraction study of this material was undertaken in collaboration with Dr. M. Cowie and Dr. B.W. Hames. The structure determination, Figure 5, proved that methylation occurred at the alkylated sulfur to produce 33a. The core atoms, Fe(1), Fe(2), S(1) and S(2), form a quasi-tetrahedral geometry which is reminiscent of the $(\mu\text{-E}_2)\text{Fe}_2(\text{CO})_6$ ($\text{E} = \text{S},^{38} \text{Se},^{39}$ and $t\text{-butylP}^{40}$) type compounds. Although the Fe-S distances in 33a, $\text{S}(2)\text{-Fe}(1) = 2.2460(9)\text{\AA}$ and $\text{S}(2)\text{-Fe}(2) = 2.2351(8)\text{\AA}$, are somewhat longer than the average of those found in $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ at $2.228(2)\text{\AA}$, the Fe-S-Fe angles compare well, $69.16(2)^\circ$ in 33a and $69.9(1)^\circ$ in $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. The Fe-C distances, $\text{Fe}(1)\text{-C}(7) = 1.923(3)$ and $\text{Fe}(2)\text{-C}(7) = 1.921(3)\text{\AA}$, are shortened with respect to 15b, $1.998(4)\text{\AA}$, with the change in geometry, as are the Fe-Fe and C-S bond lengths, Table 3. After the X-ray diffraction study of 33a was completed, the structure of a very similar compound 34 was published, Figure 6, synthesized by the reaction of di-iron nonacarbonyl and the corresponding thioketene.⁴ Table 4 compares a few of the bond lengths and angles for these two

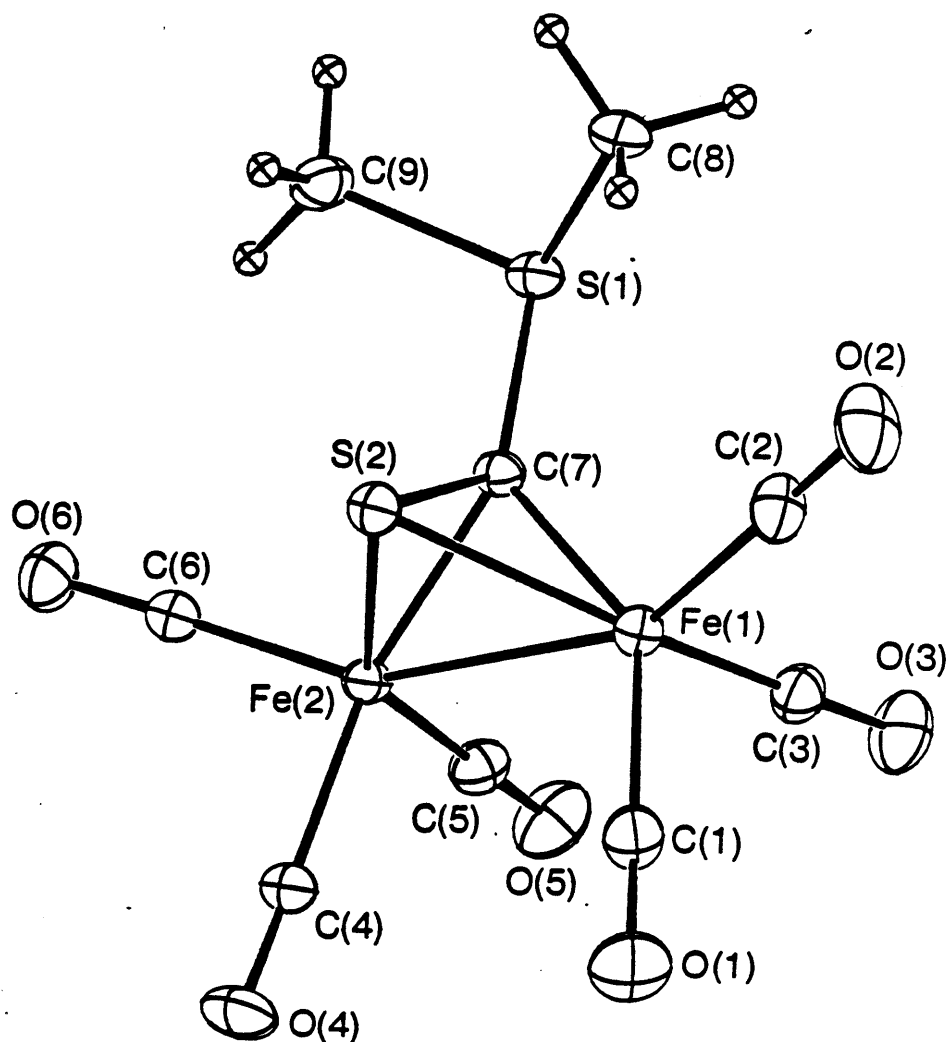


Figure 5. Perspective drawing of $(\mu, \eta^2\text{-SCS}(\text{CH}_3)_2)\text{Fe}_2(\text{CO})_6$, 33. Thermal ellipsoids are drawn at the 20% probability level except for hydrogens which are drawn artificially small.

Table 3. Some Relevant Bond Lengths (\AA) and Angles (deg) for
Compound 33a.

(i) Bond Lengths	(ii) Bond Lengths
Fe(1)-Fe(2) 2.5432(7)	C(7)-Fe(1)-S(2) 48.40(8)
Fe(1)-S(2) 2.2460(9)	C(7)-Fe(1)-Fe(2) 48.55(8)
Fe(1)-C(7) 1.923(3)	S(2)-Fe(1)-Fe(2) 55.22(2)
Fe(2)-S(2) 2.2351(8)	C(7)-S(1)-C(8) 104.8(1)
Fe(2)-C(7) 1.921(3)	C(7)-S(1)-C(9) 105.0(1)
S(1)-C(7) 1.730(3)	C(8)-S(1)-C(9) 100.3(2)
C(7)-S(2) 1.734(3)	S(2)-Fe(2)-C(7) 48.60(8)
S(1)-C(8) 1.788(3)	S(2)-Fe(2)-Fe(1) 55.62(2)
S(1)-C(9) 1.791(4)	C(7)-Fe(2)-Fe(1) 48.61(8)
	C(7)-S(2)-Fe(2) 56.20(9)
	C(7)-S(2)-Fe(1) 56.01(9)
	Fe(2)-S(2)-Fe(1) 69.16(2)
	Fe(2)-C(7)-S(2) 75.2(1)
	Fe(2)-C(7)-S(1) 135.5(2)
	S(1)-C(7)-S(2) 126.9(2)
	Fe(1)-C(7)-Fe(2) 82.8(1)
	S(1)-C(7)-Fe(1) 136.0(2)
	S(2)-C(7)-Fe(1) 75.6(1)

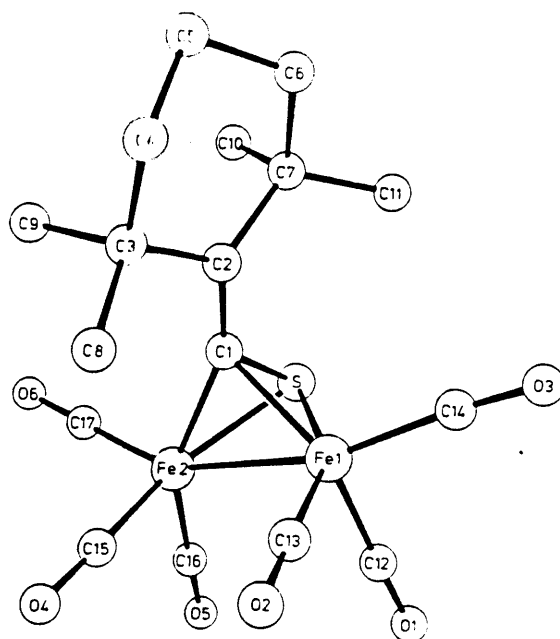


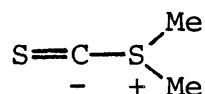
Figure 6. Structure of 34.

Table 4. Bond Lengths (\AA) and Angles (deg) for 33a⁴¹ and 34⁴.

	<u>33a</u>	<u>34</u>
Fe-Fe	2.5432 (7)	2.518 (2)
Fe-C	1.923 (3)	2.064 (9)
	1.921 (3)	1.938 (10)
Fe-S	2.2460 (9)	2.229 (3)
	2.2351 (8)	2.220 (3)
C-S	1.734 (3)	1.733 (10)
	C (7) - C (2)	C (1) - S
Fe-C-Fe	82.8 (1)	77.9 (3)
Fe-S-Fe	69.16 (2)	68.9 (1)

compounds which exhibit only minor differences.

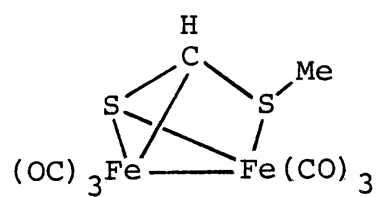
The structure of 33a confirmed that an intramolecular nucleophilic substitution occurred to displace the datively bound -SMe group, Scheme 3. Alkylation of the anionic intermediate thus formed occurs at the -SMe group to produce a sulfonium function exo to the core atoms. The intramolecular rearrangement results in the formation of a new Fe-C bond producing a μ, η^2 -thiocarbonyl moiety bridging the two $\text{Fe}(\text{CO})_3$ units perpendicular to the Fe-Fe bond. To allow each iron atom to maintain an 18-electron configuration this thiocarbonyl ligand must function as a six-electron donor. Therefore, the thio ligand can be thought of as a coordinated sulfonium ylide, 35, in which the negative charge associated with



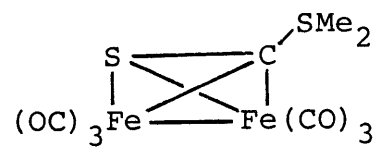
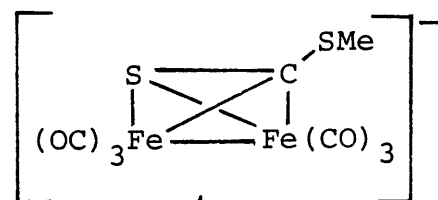
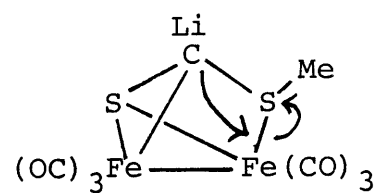
35

the carbon atom allows donation of the necessary electrons. In harmony with this concept, the C(7)-S(1) distance of $1.730(3) \text{ \AA}$ compares favorably with the C-S bond lengths found for two stabilized sulfonium ylides at 1.73^{58} and 1.707 \AA^{59} which lie between the distances for a C-S single bond (1.81 \AA)⁶⁰ and C=S double bond (1.64 \AA).⁶¹ The coordinated thio ketene of 34 can also be viewed as a dipolar ligand with a metal stabilized carbonium ion exo to the core tetrahedron. Complexes 33 and 34 represents the only two compounds structurally

Scheme 3



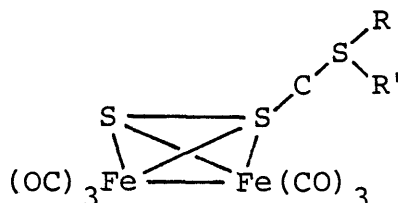
15a



33a

characterized as having a C-S moiety bound perpendicular to a metal-metal bond and which functions as a six-electron donor.

Addition of allyl bromide to the $(\mu\text{-SCHSMe})\text{Fe}_2(\text{CO})_6/\text{LDA}$ reaction mixture resulted in the isolation of 33b, mp 81-83°C, in 39% yield. In like manner, $(\mu\text{-SCHSEt})\text{Fe}_2(\text{CO})_6$ also could be deprotonated at -78°C with LDA to produce a red-brown reaction mixture. Addition of iodomethane or iodoethane to such a solution allowed the formation of 33c and 33d in 84 and 45%



33a, R=R'=Me

33b, R=Me, R'=CH₂CH=CH₂

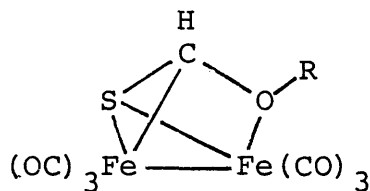
33c, R=Me, R'=Et

33d, R=R'=Et

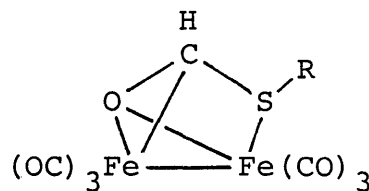
yield, respectively. Like the simple dimethyl derivative, 33a, all of these compounds were orange, air-stable solids, only slightly soluble in pentane but very soluble in methylene chloride and chloroform. The ¹³C NMR spectra of 33b, c, and d also contained peaks assignable to the bridging thiocarbonyl carbon in the same area as observed for 33a: δ_{C} 101.5(33b), 102.1(33c) and 99.9(33d), and like 33a the carbonyl ligands appeared as a single peak for each compound.

Given the unexpected chemical properties of the $\text{Fe}_2(\text{CO})_6$

coordinated allyl dithioformates⁴¹ it was wondered if the mono-oxo analogs, 36 and 37, could be made and if they would



36

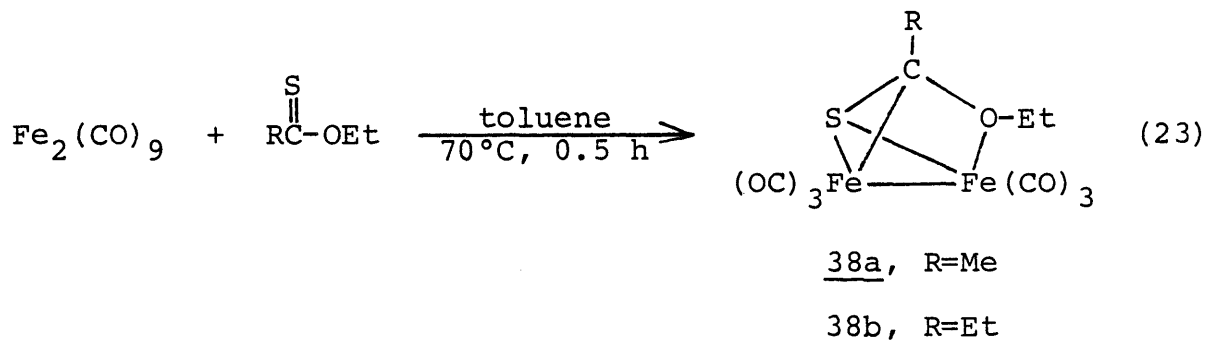


37

display similar chemical behavior. A synthetic strategy leading to either of these compounds seemed well grounded in the work of Alper and Patin, (eq.1 and 2). In fact, Patin et al. had actually reported the reaction of two O-alkyl thioformates, HC(S)OR (R = cholestanyl, cholesteryl), with $\text{Fe}_2(\text{CO})_9$ as giving complexes of structure 36, but no structural data were given to substantiate this.^{6b} Alper and Foo had shown that O-alkyl thiobenzoates also would react with $\text{Fe}_2(\text{CO})_9$ yielding diiron hexacarbonyl complexes with the ester coordinated as in 36.² Thus it was felt with confidence that O-ethyl thioformate could be used as starting material in the synthesis of 36 (R = Et).

Since Alper and Foo had only concerned themselves with the O-alkyl thiobenzoates, it seemed worth the effort to react O-ethyl thioacetate and O-ethyl thiopropanoate with diiron nonacarbonyl to determine if they would coordinate in the same manner. Both thioesters were allowed to react with a slight excess of $\text{Fe}_2(\text{CO})_9$ in toluene at 70°C for 30 min. Removal of the solvent, followed by filtration chromatography (silicic

acid/pentane), resulted in the isolation of slightly air-sensitive, black-red solids in 30% yield in both reactions. The combustion analyses and field desorption mass spectra indicated that the compounds were $(RC(S)OEt)Fe_2(CO)_6$ complexes. The IR spectra (pentane) of these two compounds revealed seven lines in the terminal $\nu(CO)$ region, in harmony with the spectra reported previously by Alper for the O-alkyl thiobenzoate compounds.² The ^{13}C NMR spectra showed two poorly resolved signals for the carbonyl ligands, very similar to those in the ^{13}C NMR spectra of the alkyl dithioformate complexes 15. Based on these data, these two new compounds have been assigned structure 38, (eq.23). The ^{13}C NMR spectra also revealed that the

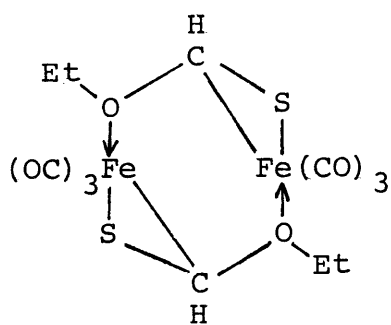


ester thiocarbonyl carbons are shifted approximately 96 ppm upfield upon coordination (Table 5), a phenomenon also noted by Patin for the related dithioester complexes.³

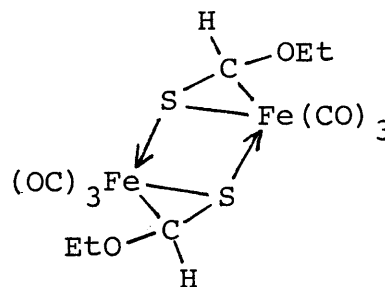
Using the same experimental procedure, O-ethyl thioformate was treated with an excess of diiron nonacarbonyl in toluene under nitrogen. The solution was heated using an oil bath at 70°C and stirred for 3 h. After removal of the

solvent, the solid material remaining was crystallized from pentane at -20°C to give red-brown, air-stable crystals, mp $\sim 100^{\circ}\text{C}$ dec, in 54% yield. The ^1H NMR data confirmed that this material contained a coordinated O-ethyl thioformate ligand; the thioformyl proton singlet occurred at δ 7.18, integrating for one proton. The ethyl group signals appeared as a triplet δ 1.31 ($J = 7.0\text{Hz}$), for the CH_3 group but as a complex multiplet for the methylene unit which collapsed to an AX quartet, δ 4.13 and 3.96; $J_{\text{AX}} = 9.2\text{Hz}$, when the methyl protons were decoupled. This indicated that the product was chiral which was expected for a compound with structure 36. However, the IR spectrum (in pentane) showed only three bands in the terminal carbonyl region, in stark contrast to the seven lines observed for compounds 38. The ^{13}C NMR spectrum did not harmonize with the expected structure either since the carbonyl carbons appeared as three sharp signals at δ_{C} 210.1, 207.9, and 202.0, Table 5, although the thiocarbonyl carbon signal was shifted upfield as in 38a and 38b. Of significance was the field desorption mass spectrum which showed $M^+ = 460$. This corresponded to a formulation of $[\text{HC}(\text{S})\text{OEt}]_2\text{Fe}_2(\text{CO})_6$ which the combustion analysis also confirmed.

Two structural possibilities, 39 and 40, seemed most likely for $[\text{HC}(\text{S})\text{OEt}]_2\text{Fe}_2(\text{CO})_6$. In both the O-ethyl thioformate ligand acts as a four-electron donor; the difference being that in 39 the ethoxy oxygen is coordinated. However, complex 40 was favored since dialkylthioketenes have been reported to form such complexes when treated with diiron



39



40

nonacarbonyl.^{4a} Dr. M. Cowie and Dr. B.W. Hames provided confirmation of the product as 40 with an X-ray diffraction study, Figure 7.

The molecule consists of two inversion-related iron centers in which there is no Fe-Fe bond, rather two bridging O-ethyl thioformate groups hold the $\text{Fe}(\text{CO})_3$ units together. The Fe-Fe separation of $3.483(1)\text{\AA}$ is outside the range of normal iron-iron bonds and can be contrasted to the Fe-Fe distances in complexes 16 ($2.485(1)\text{\AA}$), 15b ($2.627(1)\text{\AA}$) and 33 ($2.5432(7)\text{\AA}$). The thiocarbonyl function of each thioformate is side-on bonded to one iron and is bound to the other iron by a dative bond from the sulfur atom. Thus each O-ethyl thioformate ligand acts as a four-electron donor without any interaction between the ethoxy group and the metals. This unexpected mode of coordination for the thioformate did not affect the Fe-C distance ($1.987(3)\text{\AA}$) much as compared to 15b ($1.998(4)\text{\AA}$) which also has a side-on bonded thiocarbonyl group. Overall each iron atom has a quasi-octahedral geometry if the C-S unit is considered as occupying two coordination sites.

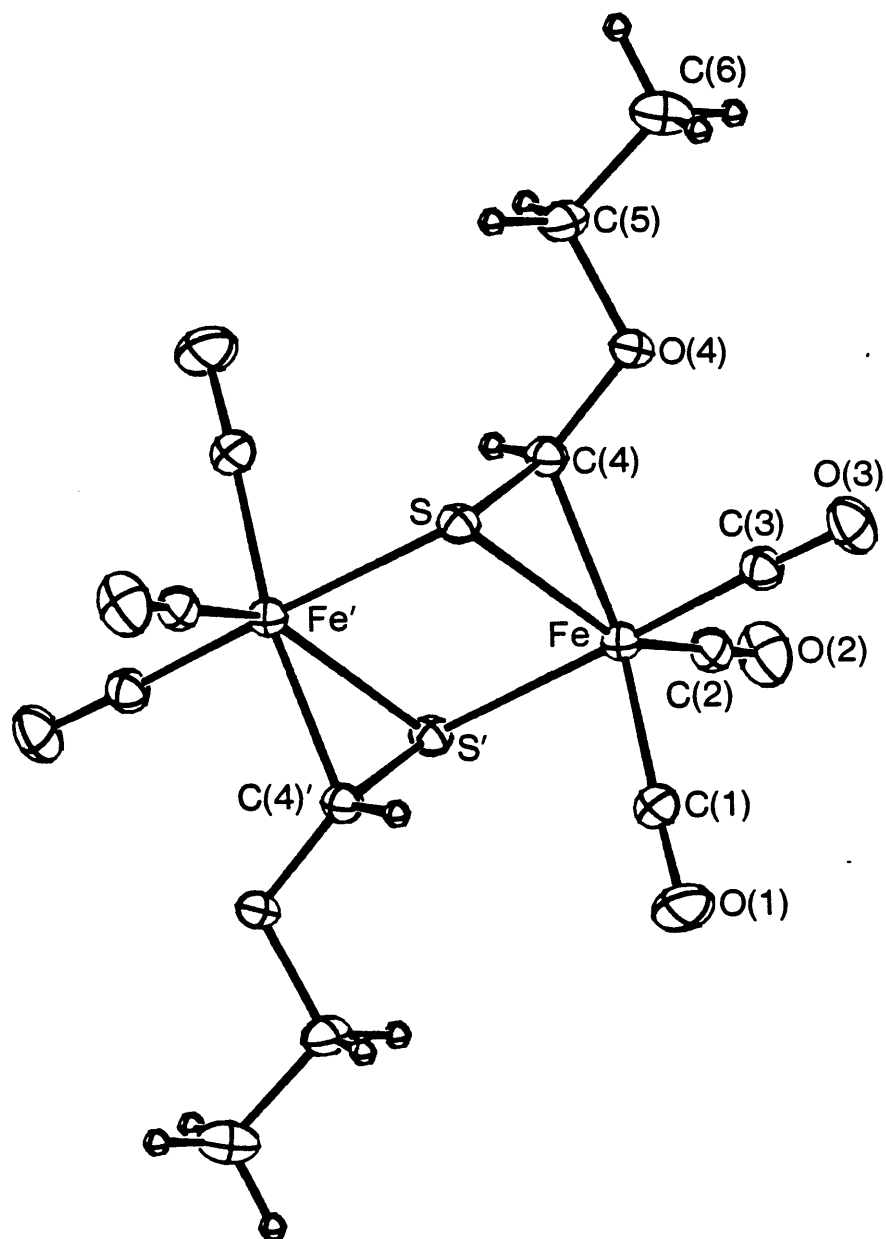


Figure 7. Perspective view of $(\text{HC}(\text{S})\text{OEt})_2\text{Fe}_2(\text{CO})_6$ showing the numbering scheme. Primed atoms are related to unprimed ones by the inversion center at the center of the complex.

Table 6. Selected Interatomic Distances (\AA) and Angles (deg) for Compound 40.

(i) Bond Lengths

Fe-S	2.2810(9)	C(1)-O(1)	1.122(3)
Fe-S'	2.3146(9)	C(2)-O(2)	1.125(3)
S-C(4)	1.774(3)	C(3)-O(3)	1.125(4)
Fe-C(1)	1.813(3)	C(4)-O(4)	1.374(3)
Fe-C(2)	1.785(3)	O(4)-C(5)	1.429(3)
Fe-C(3)	1.794(3)	C(5)-C(6)	1.479(5)
Fe-C(4)	1.987(3)		

(ii) Non-Bonded Contacts

Fe-Fe'	3.483(1)	Fe-C(4)'	3.188(3)
S-S'	2.999(1)	H(C4)-C(1)'	2.59 ^a

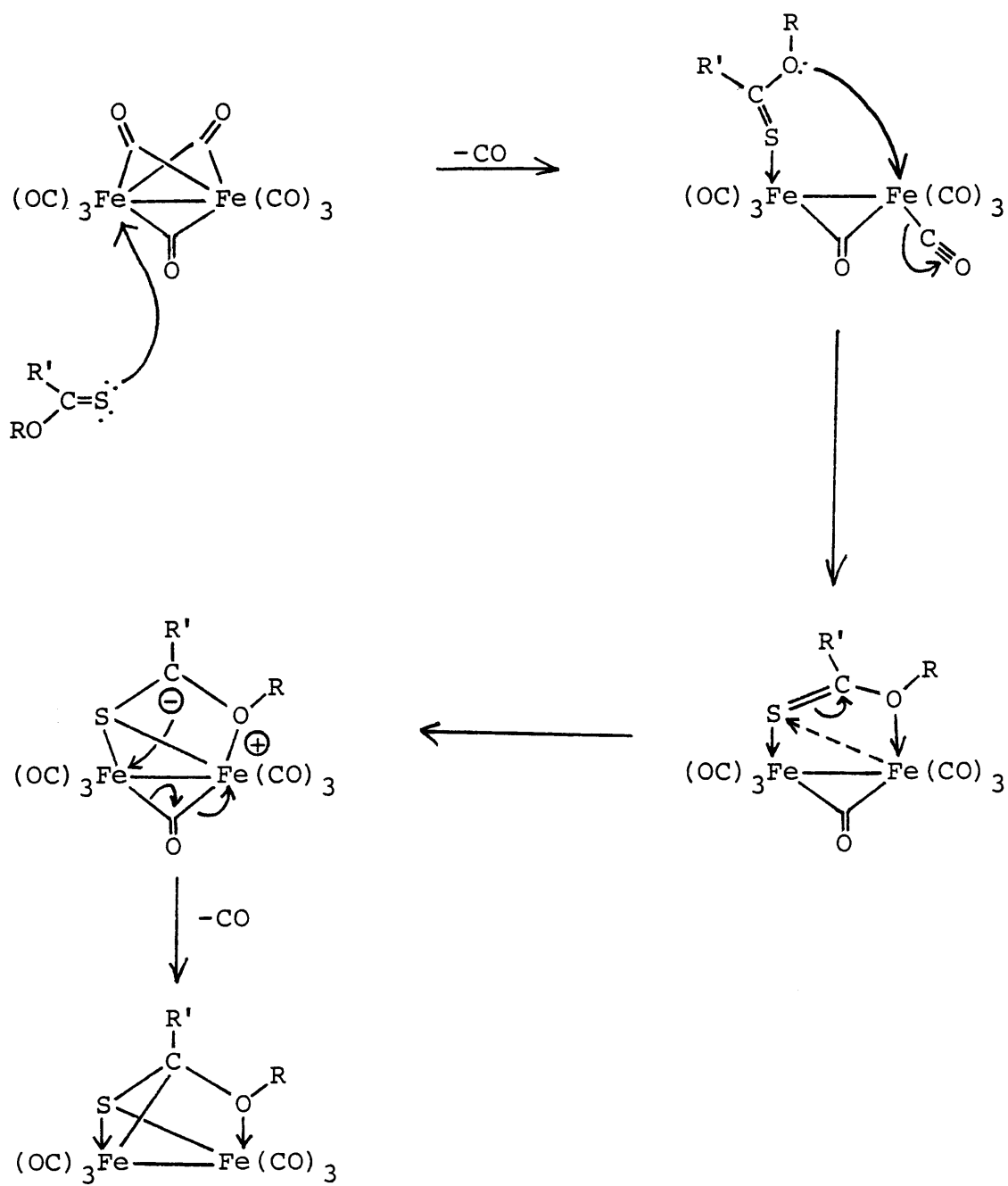
(iii) Bond Angles

C(1)-Fe-C(2)	102.6(1)	C(4)-Fe-S'	90.57(8)
C(1)-Fe-C(3)	90.7(1)	S-Fe-S'	81.45(3)
C(1)-Fe-C(4)	161.2(1)	Fe-C(1)-O(1)	177.5(3)
C(1)-Fe-S	112.8(1)	Fe-C(2)-O(2)	178.0(3)
C(1)-Fe-S'	88.6(1)	Fe-C(3)-O(3)	178.1(3)
C(2)-Fe-C(3)	93.5(1)	Fe-S-Fe'	98.55(3)
C(2)-Fe-C(4)	96.2(1)	Fe-S-C(4)	57.06(8)
C(2)-Fe-S	143.3(1)	Fe'-S-C(4)	101.67(9)
C(2)-Fe-S'	90.5(1)	Fe-C(4)-S	74.4(1)
C(3)-Fe-C(4)	88.8(1)	Fe-C(4)-O(4)	116.9(2)
C(3)-Fe-S	95.23(9)	S-C(4)-O(4)	115.4(2)
C(3)-Fe-S'	176.05(9)	C(4)-O(4)-C(5)	112.8(2)
C(4)-Fe-S	48.51(7)	O(4)-C(5)-C(6)	108.8(3)

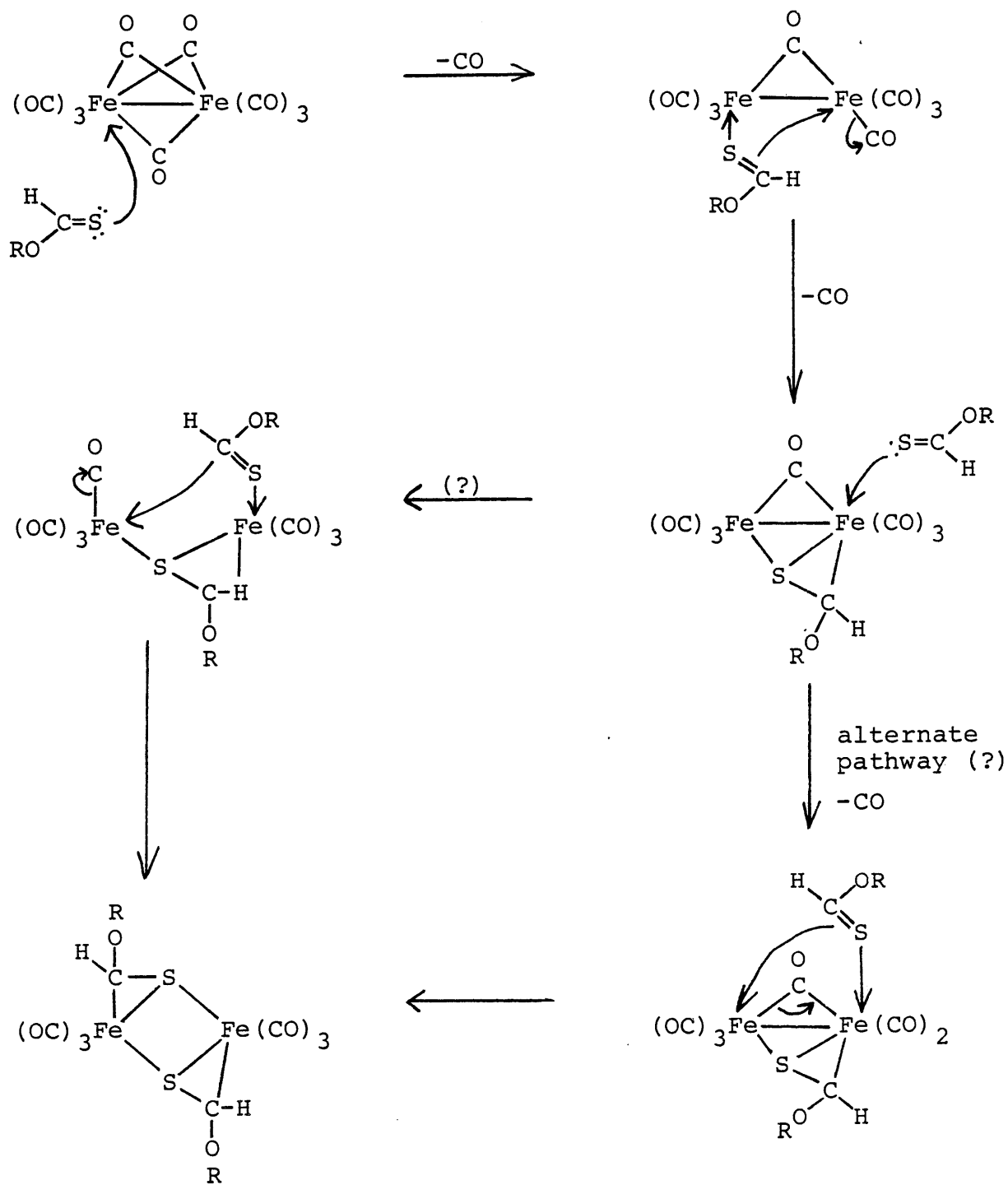
^aH(C4) is the hydrogen atom on C(4).

A mechanism to rationalize the formation of complexes of 1 (eq.1) from the reactions of ArC(S)OR and $\text{Fe}_2(\text{CO})_9$ has been proposed by Alper and Foo, Scheme 4. However, the reaction of O-ethyl thioformate with $\text{Fe}_2(\text{CO})_9$ must necessarily proceed by a different mechanism, although the first step, nucleophilic attack by sulfur at an iron atom very likely is the same. Examination of the structure of 40 gives insight as to what the mechanistic differences may be. A rather short contact of 2.59\AA exists between $\text{C}(1)'$ and the hydrogen atom on $\text{C}(4)$. This being the case, coordination, as in 40, of a thiocarbonyl containing molecule cannot occur if two groups bulkier than hydrogen are attached to the thiocarbonyl carbon ($\text{C}(4)$ in 40) owing to the highly unfavorable non-bonded contact which would result. The reasonable second step (after nucleophilic attack of sulfur at iron) in the formation of 40 would be π -coordination of the thiocarbonyl function to the second metal, Scheme 5. In view of the thiophilicity of iron this step is probably favored over coordination of the harder oxygen atom. However, in the reactions of the monothioesters ($\text{R}'\text{C(S)OR}$) where $\text{R}' \neq \text{H}$ this step is sterically prohibited, as discussed above, thus forcing coordination of the oxygen atoms. When this occurs, the ester ultimately functions as a six-electron donor which together with the Fe-Fe bond and carbonyl ligands give the metals their 18-electron configuration. However, in a dinuclear molybdenum system coordination of thioketenes and monothioesters does occur as in 40.^{42,43} In the case of O-ethyl thioformate, π -coordination of the C=S moiety results

Scheme 4

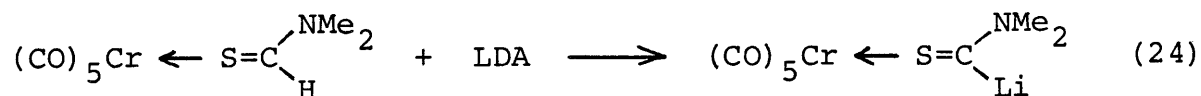


Scheme 5



in a bridging four-electron donor, presumably giving a 1:1 adduct as shown in Scheme 5. This species, apparently still vulnerable to attack by a second HC(S)OEt molecule, forms a 2:1 adduct, with loss of CO, in which there is no Fe-Fe bond.

Although the reaction of O-ethyl thioformate and $\text{Fe}_2(\text{CO})_9$ did not result in the formation of 36 as expected, the isolated product 40 did contain two O-ethyl thioformate ligands and removal of a formyl proton from one of these ligands was still attempted. In a related report it was shown that a coordinated thioformamide ligand could be deprotonated with LDA, (eq. 24).⁴⁴ Addition of LDA to a red, THF solution of 40 caused a

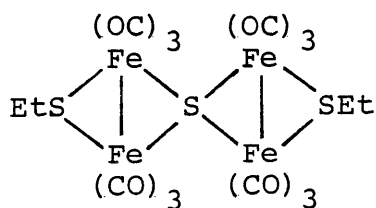


color change to brown. Iodomethane was added after 30 min and the reaction mixture warmed to room temperature. However, the color of the solution remained brown and TLC analysis of the mixture showed no products or starting material. No products could be isolated from the reaction.

Examination of the literature indicated that, just as little had been done in the way of studying the reactions of O-alkyl thioesters and thioformates with iron carbonyls, nothing had been done with the isomeric S-alkyl thioesters. Their inclusion in this study was of interest to contrast the reactivity of these two classes of organosulfur molecules. Although similar in elemental composition, they differ in the

key function of the carbonyl group. As already reported, the O-alkyl thioesters react with diiron nonacarbonyl to yield complexes in which the intact ester, coordinates via the thio-carbonyl moiety in a π side-on fashion as in 38 and 40. This form of reactivity is unlikely for the S-alkyl thioesters.

S-ethyl thioformate (6.77 mmol) in toluene was stirred with $\text{Fe}_2(\text{CO})_9$ (8.25 mmol) at room temperature for 17 h. Analysis of the mixture by TLC indicated that no product formation had occurred, so the solution then was heated in an oil bath at 70°C for 1 h. After this treatment two products were isolated. The major product proved to be the e,a isomer of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ isolated in 15% yield based on the amount of ester consumed. The other product, which showed no resonances in its ^1H NMR spectrum, due to a formyl type proton, was identified as the tetrametallic complex 41, mp 154-156°C



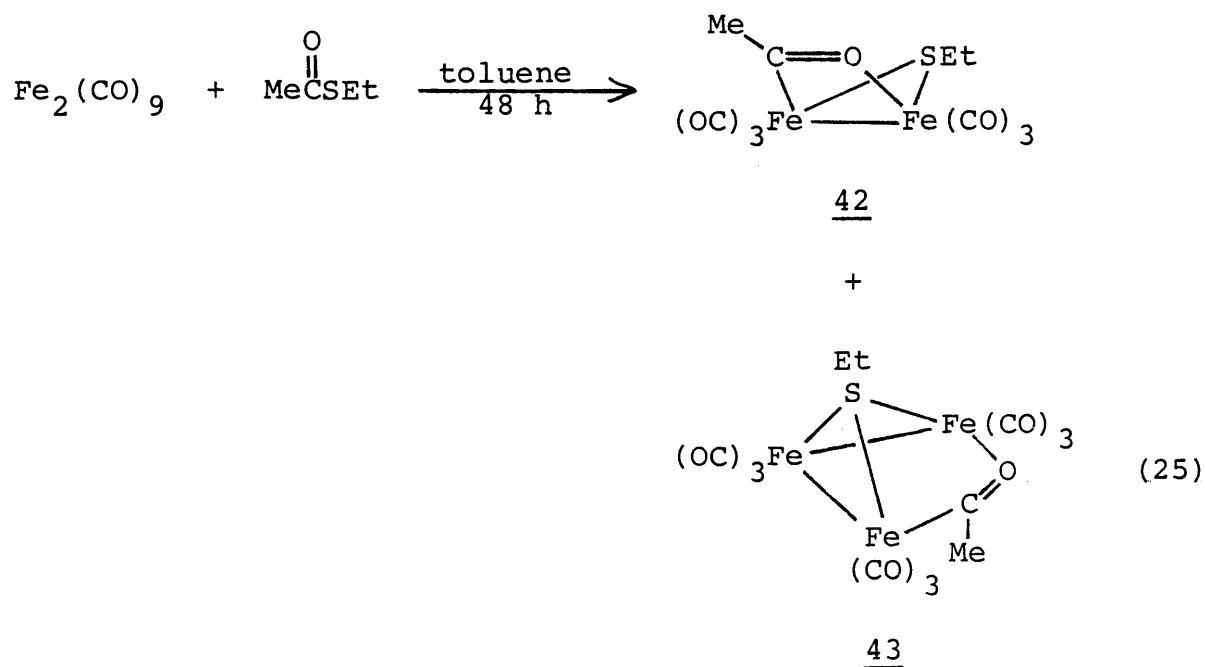
41

dec, isolated in 7% yield. Thus the reaction between diiron nonacarbonyl and S-ethyl thioformate resulted in the isolation of products in which deformylation of the thioester had occurred. Tetranuclear complexes such as 41 have been isolated previously and in two cases crystal structure determinations were

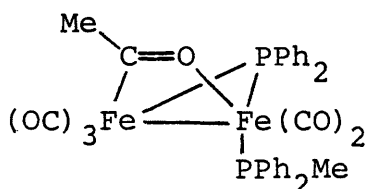
performed which showed the alkyl groups to occupy equatorial positions.⁴⁵ The ^1H NMR spectrum of 41 revealed that the two ethyl groups in the complex were equivalent and, in harmony with the previous structural studies, no doubt both occupy equatorial positions. In a similar reaction to that reported here, an asymmetric complex of type 41 was formed in the decarbonylation of a dithiocarbonate when it was treated with $\text{Fe}_2(\text{CO})_9$.^{45d}

S-Ethyl thioformate obviously did not react with $\text{Fe}_2(\text{CO})_9$ in a manner analogous to O-ethyl thioformate nor did it lead to the isolation of 37. Still, the reactions of other S-alkyl thioesters were of interest to determine if they too would fragment in a similar manner when treated with $\text{Fe}_2(\text{CO})_9$. S-Ethyl thioacetate (6.0 mmol) in toluene and diiron nonacarbonyl (8.25 mmol) were stirred for 48 h at room temperature. Separation of the two major products was achieved by filtration chromatography [silicic acid; eluting with 9/1 (v/v) pentane/ CH_2Cl_2]. The first product which eluted from the column was a dark red oil, 42, a diiron hexacarbonyl complex isolated in 13% yield. The second band gave a red-black solid in 10% yield which, by its mass spectrum and combustion analysis, was determined to be a triiron nonacarbonyl species, 43. Both compounds had formed via the incorporation of only one thioester per molecule. However, coordination of the thioester did not appear to have occurred in the same manner as found in 38 or 40. NMR data for 42 revealed the presence of two isomers and although no isomers existed for 43, the downfield signal of the ester

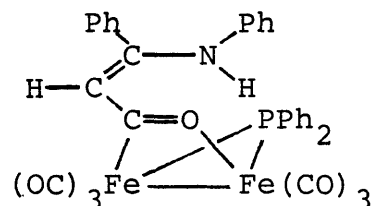
carbonyl carbon (δ_C 317.5) in its ^{13}C NMR spectrum indicated that it was bound to the metals in the same manner as in 42 (δ_C 299.2 and 301.9). Unlike the coordinated O-alkyl mono-thioesters for which an upfield shift of the coordinated thiocarbonyl carbon was found in their ^{13}C NMR spectra, the ester carbonyl shifts in 42 and 43 are moved a little over 100 ppm downfield from the δ_C 194.7 of the original ester, Table 7. Large downfield shifts for the thiocarbonyl carbons of tri-thiocarbonates⁸ and xanthates⁶ after reaction with $\text{Fe}_2(\text{CO})_9$ have been reported by Patin et al., who have shown it to be the result of a fragmentation of the organic starting material, (eq.3 and 4). Thus the spectral data for 42 and 43 can be explained in terms of the formation of bridging acyl complexes, (eq.25). The far downfield acyl carbon signals in the ^{13}C NMR



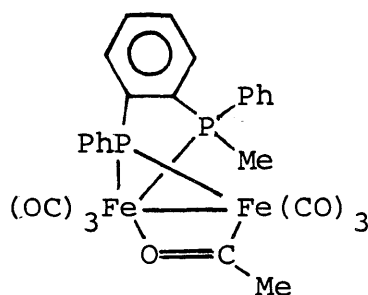
spectra are in the region reported for other bridging acyl ligands, δ_C 253 to 323.⁴⁶ The presence of acyl ligands is further supported by the strong intensity bands, relative to the C-H deformation bands in the same region at 1512 and 1497 cm^{-1} in the IR spectra corresponding to the $\nu(\text{CO})$ acyl stretching frequencies of 42 and 43, respectively.^{46,47} A few examples of acyl ligands bridging two iron atoms in complexes similar to 42 have been reported; 44,^{46a} 45,^{46d} 46^{48a} and 47.^{48b}



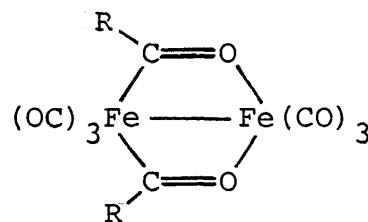
44



45



46



47

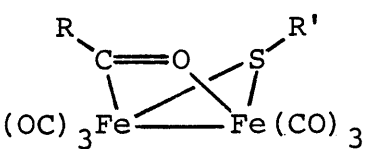
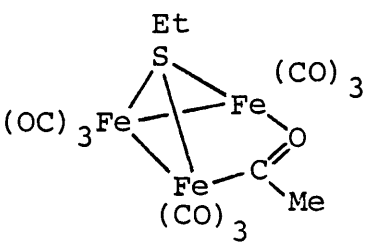
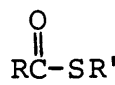
In 43 the acyl ligand bridges the two nonbonded iron atoms of an $\text{Fe}_3(\text{CO})_9$ complex with a tricapping ethanethiolate ligand. It has been assigned this structure since Huttner has reported the isolation of structurally similar complexes, albeit none in which the bridging group is an acyl ligand.⁴⁹

The isomers of 42 now can be explained conveniently in terms of the orientation of the ethyl group as axial (a) or equatorial (e). The ^1H NMR spectrum showed two triplets at δ 1.37 ($J = 7.3\text{Hz}$) and 1.48 ($J = 7.3\text{Hz}$), the higher field signal corresponding to the axial ethyl group. Integration of these two triplets allowed an isomer ratio of 3.6/1 (e/a) to be determined. Two signals also were observed for the acyl methyl groups at δ 2.25 (e) and 2.31 (a). (The letters e and a refer to the orientation of the ethyl group.) The methylene protons for both isomers are diastereotopic, due to the chiral framework, of the complexes and appear as a complex multiplet at δ 2.57.

Using the same procedure described for S-ethyl thioacetate, S-ethyl thiobenzoate and thiopivalate were also treated with diiron nonacarbonyl. However, from these reactions only the bimetallic products, $(\mu\text{-RCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, were isolated in 16% ($R = \text{Ph}$) and 10% ($R = \text{t-butyl}$) yield. The bridging pivaloyl complex, mp $36\text{-}38^\circ\text{C}$, was isolated as only one isomer with an equatorial ethyl group; the benzoyl product, mp $81\text{-}86^\circ\text{C}$, was isolated as a mixture of both isomers, 4.4/1 (e/a).

It was later discovered that the dinuclear acyl complexes also could be formed in the reaction between S-alkyl thioesters and $\text{Fe}_3(\text{CO})_{12}$. The reaction between S-ethyl thioacetate and $\text{Fe}_3(\text{CO})_{12}$ did not occur at room temperature after 24 h in toluene. However, after heating this solution for 22.5 h at 75°C , 42 could be isolated in 55% yield as a mixture of both isomers 2.5/1 (e/a). Using the same reaction conditions S-ethyl

Table 7. ^{13}C NMR^a and IR^b Data of Acyl Complexes.

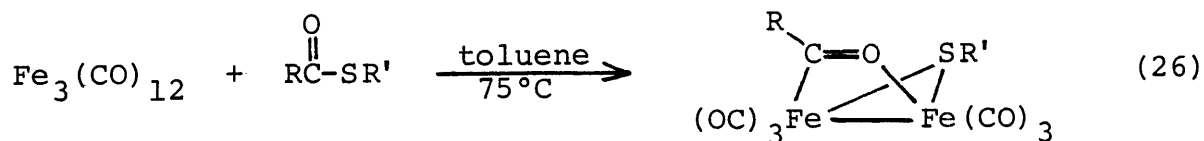
Compound	R	R'	δ_{C} (acyl)	ν (acyl CO)
	CH ₃	CH ₃ ^c	298.9	1503
	CH ₃	CH ₂ CH ₃	299.2 (e) 301.9 (a)	1512
	Ph	CH ₂ CH ₃	289.0 (e) 291.6 (a)	1470
			317.5	1497
	CH ₃	CH ₃	195.2	
	CH ₃	CH ₂ CH ₃	194.7	
	Ph	CH ₂ CH ₃	190.9	

^aMeasured in CDCl₃ solution and reported in ppm downfield from tetramethylsilane.

^bMeasured in CHCl₃ solution.

^cMeasured in C₆D₆ solution.

thiobenzoate, S-ethyl thiopivalate and S-methyl thioacetate also were allowed to react with $\text{Fe}_3(\text{CO})_{12}$. Diiron hexacarbonyl acyl complexes also were isolated, although in lower yields than that of 42, (eq.26). For these reactions nearly stoichio-



R = R' = Me, 27%

R = Ph, R' = Et, 26%

R = t-butyl, R' = Et, 11%

metric amounts of the thioester and $\text{Fe}_3(\text{CO})_{12}$ were used. The use of a two-fold excess of S-ethyl thiobenzoate, however, did not increase the yield of the acyl complex which was obtained in 24% yield.

Experimental Section

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone ketyl. Carbon disulfide was distilled from phosphorus pentoxide. Reagent grade pentane and dichloromethane were deoxygenated by bubbling nitrogen through them for 15 min prior to use. The gem-dithiols²³ and thioesters; HC(S)OEt ,⁵⁰ RC(S)OEt ,⁵¹ HC(O)SEt ⁵² and RC(O)SR' ,⁵³ were synthesized following literature procedures as were $\text{Fe}_2(\text{CO})_9$ ⁵⁴ and $\text{Fe}_2(\text{CO})_{12}$.⁵⁵

Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 ml) in a 350 ml glass-frit filter funnel, was used in most cases. Column chromatography was performed with a 350 x 25 mm column using silicic acid. All chromatography was done without exclusion of atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at -20°C .

Infrared spectra were obtained using a Perkin-Elmer Model 457A or Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JeolFX-90Q or a Bruker 250 NMR spectrometer operating at 90MHz and 250MHz, respectively. ^{13}C NMR spectra were obtained using a JeolFX-90Q or Bruker 270 NMR instrument operating at 22.5MHz and 67.9MHz, respectively. Mass spectra were obtained with a Varian MAT-44 or a Finnigan-3200 spectrometer operating at 70eV. Field

desorption mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Melting points of analytically pure samples were obtained on a Buchi Melting Point Apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Preparation of Methanedithiol.²³ (GBW-VII-62).

Caution: All work connected with this experiment should be conducted in a well ventilated hood.

A 1000 ml, three-necked, round-bottomed flask equipped with a stir-bar and reflux condenser was charged with 33.7 g (600 mmol) of KOH and 500 ml of ethanol. To this solution, 42.9 ml (600 mmol) of thiolacetic acid (Aldrich) was added and the mixture was stirred for 15 min. Dibromomethane, 33.9 ml (300 mmol), then was added and the solution refluxed for 2 h. A white precipitate formed. The solution was filtered after cooling to room temperature and the ethanol removed under reduced pressure leaving a yellow oil. This oil was taken up in a CH_2Cl_2 and washed with water. The organic layer was dried over MgSO_4 and filtered. The CH_2Cl_2 was removed giving 41 g (249 mmol, 83% yield) of $\text{H}_2\text{C}(\text{SC}(\text{O})\text{Me})_2$ as a yellow oil which was used without further purification.

^1H NMR (CDCl_3 , 90MHz): δ 2.26 (s, 6H, CH_3) and 4.14 (s, 2H, CH_2).

The above yellow oil was dissolved in 250 ml of a 2% HCl methanol solution (w/v) which was stirred overnight. The

mixture was then transferred to a separatory funnel and 200 ml of water added. This was extracted with 20 ml of CH_2Cl_2 . The organic layer was dried over MgSO_4 and filtered. The CH_2Cl_2 was boiled off at atmospheric pressure and the remaining yellow oil distilled at reduced pressure. Methanedithiol was collected as a colorless liquid at $\sim 50^\circ\text{C}$, 90 mmHg (lit.⁵⁷; 58°C , 80 mmHg); 10.6 g (132.6 mmol, 44% yield based on CH_2Br_2).

^1H NMR (CDCl_3 , 90MHz): δ 2.23 (t, 2H, $J = 7.8$ SH) and 3.61 (t, 2H, $J = 7.8$ CH_2).

Reaction Between Triiron Dodecacarbonyl and Methanedithiol.

(GBW-VII-61).

A 250 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 4.53 g (9.0 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and flushed with nitrogen. THF (50 ml) of 0.71 g (8.86 mmol) of $\text{H}_2\text{C}(\text{SH})_2$ ²³ were added by syringe and the mixture was refluxed gently for 1 h. The solvent was removed and the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 2.71 g (7.57 mmol, 85% yield based on $\text{H}_2\text{C}(\text{SH})_2$) of $(\mu\text{-CH}_2\text{S}_2)\text{Fe}_2(\text{CO})_6$ as an air-stable red solid, mp $74\text{--}76^\circ\text{C}$ (lit.⁶² mp $74\text{--}76^\circ\text{C}$) after crystallization from pentane. It was identified by comparison of its ^1H NMR and IR spectra to those reported in the literature.^{13,62}

IR (pentane) (terminal carbonyl region): 2081(s), 2041(vs), 2010(vs), 2001(vs), 1990(m), 1960(w) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 4.61.

For an alternate synthesis, see reference 62.

Reaction Between (μ -Methanedithiolato)bis(tricarbonyliron),
Lithium Diisopropylamide and Iodomethane. (GBW-VI-71,
LCS-III-26).

A 250 ml, round-bottomed, three-necked flask equipped with a magnetic stir-bar and serum caps was charged with 0.837 g (2.34 mmol) of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ and flushed with nitrogen. THF (50 ml) was added and the red solution cooled to -78°C . Lithium diisopropylamide (2.50 mmol) in 10 ml of THF was added causing a color change to green. The reaction mixture was stirred for 15 min, then 1.0 ml (16.1 mmol) of MeI (Aldrich) was added. The solution was removed from the cold bath and stirred for 1 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in pentane/ CH_2Cl_2 (4/1, v/v). This solution was filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to column chromatography (silicic acid/pentane). Pentane eluted a minor yellow band of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ and pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 0.678 g (1.82 mmol, 78% yield) of $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil.

IR (pentane) (terminal carbonyl region): 2076(s), 2031(vs), 2006(vs), 1994(s), 1982(m), 1975(m) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 2.33 (s, 3H, CH_3), 3.89 (s, 1H, S_2CH).

^{13}C NMR (CDCl_3 , 22.5MHz): δ_{C} 35.4 (q, $J = 14\text{Hz}$, CH_3), 55.4 (d, $J = 188\text{Hz}$, S_2CH), 208.0 (broad, CO) and 211.2 (s, CO).

Mass spectrum, m/z (relative intensity): 372 (M^+ , 3), 344 ($M^+ - CO$, 2), 316 ($M^+ - 2CO$, 5), 288 ($M^+ - 3CO$, 5), 260 ($M^+ - 4CO$, 8), 232 ($M^+ - 5CO$, 27), 204 ($M^+ - 6CO$, 42), 189 (Fe_2S_2CH , 21), 176 (Fe_2S_2 , 52), 144 (Fe_2S , 58), 112 (Fe_2 , 31), 88 (FeS , 19), 56 (Fe , 100).

Anal. Calcd. for $C_8H_4Fe_2O_6S_2$: C, 25.83; H, 1.08%.

Found: C, 26.09; H, 1.16%.

Reaction Between (μ -Methanedithiolato)bis(tricarbonyliron),
Lithium Diisopropylamide and 1-Bromo-2-propanone. (GBW-V-74).

Lithium diisopropylamide, 2.10 mmol, was added to 0.70 g (1.95 mmol) of $(\mu-H_2CS_2)Fe_2(CO)_6$ in 50 ml of THF at $-78^\circ C$ producing a green reaction mixture. After the latter had been stirred for 20 min at $-78^\circ C$, 0.5 ml (5.96 mmol) of 1-bromo-2-propanone was added. The solution was stirred for 0.5 h at $-78^\circ C$ and 2.5 h at room temperature during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in pentane/ CH_2Cl_2 (4/1, v/v). The solution was filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to column chromatography (florisil/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 0.447 g (1.08 mmol, 55% yield) of $(\mu-SCHSCH_2C(O)CH_3)Fe_2(CO)_6$ as an air-stable red solid, mp $80-82^\circ C$ after recrystallization from pentane/ CH_2Cl_2 .

IR ($CHCl_3$): 1715(s) ($C=O$), 1375(sh), 1360(m), 1270(m), 1143(m), 970(w), 610(s), 555(s) cm^{-1} ;

terminal carbonyl region ($CHCl_3$): 2070(s), 2015(vs), 2003(vs),

1994(s) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 2.23 (s, 3H, CH_3), 3.50, 3.69 (AXq, $J = 15.9\text{Hz}$, 2H, SCH_2), 3.94 (s, 1H, S_2CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 29.4 (q, $J = 128\text{Hz}$, CH_3), 53.4 (d, $J = 190\text{Hz}$, S_2CH), 62.0 (t, $J = 140\text{Hz}$, CH_2), 199.4 (s, ketone CO), 208.3 (br, CO), and 210.9 (s, CO).

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{Fe}_2\text{O}_7\text{S}_2$: C, 29.01; H, 1.46%.

Found: C, 28.96; H, 1.61%.

Reaction Between (μ -Methanedithiolato)bis(tricarbonyliron),
Lithium Diisopropylamide and Iodoethane. (GBW-VI-58, LCS-III-33).

Lithium diisopropylamide, 2.10 mmol, was added to 0.70 g (1.95 mmol) of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ in 50 ml of THF at -78°C producing a green reaction mixture. This was stirred for 20 min, and then 1.5 ml (18.75 mmol) of iodoethane (Aldrich) was added. The solution was removed from the cold bath and stirred for 1.5 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in pentane/ $\text{CH}_2\text{-Cl}_2$ (4/1, v/v) and filtered through a pad of silicic acid. After removal of solvent, it was subjected to column chromatography (silicic acid/pentane). Pentane eluted a minor yellow band of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ and pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which yielded 0.51 g (1.32 mmol, 68% yield) of $(\mu\text{-SCHSCH}_2\text{CH}_3)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil.

IR (pentane) (terminal carbonyl region): 2075(s), 2027(vs), 2003(vs), 1992(s), 1980(m), 1974(m) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 1.25 (t, $J = 7.3\text{Hz}$, CH_3), 2.63 (m, 2H, SCH_2) and 3.97 (s, 1H, S_2CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 11.8 (q, $J = 128\text{Hz}$, CH_3), 46.2 (t, $J = 141\text{Hz}$, SCH_2), 52.2 (d, $J = 188\text{Hz}$, S_2CH), 208.8 (br, CO) and 211.3 (s, CO).

Mass spectrum, m/z (relative intensity): 386 (M^+ , 15), 358 ($\text{M}^+ - \text{CO}$, 12), 330 ($\text{M}^+ - 2\text{CO}$, 29), 302 ($\text{M}^+ - 3\text{CO}$, 24), 274 ($\text{M}^+ - 4\text{CO}$, 29), 246 ($\text{M}^+ - 5\text{CO}$, 67), 218 ($\text{M}^+ - 6\text{CO}$, 89), 190 ($\text{Fe}_2\text{S}_2\text{CH}_2$, 39), 189 ($\text{Fe}_2\text{S}_2\text{CH}$, 46), 188 ($\text{Fe}_2\text{S}_2\text{C}$, 26), 176 (Fe_2S_2 , 63), 144 (Fe_2S , 100), 112 (Fe_2 , 24), 88 (FeS , 12), 56 (Fe , 61).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$: C, 28.00; H, 1.57%.

Found: C, 28.31; H, 1.67%.

Reaction Between (μ -Methanedithiolato)bis(tricarbonyliron), Lithium Diisopropylamide and Benzyl Chloride. (GBW-VI-74).

Lithium diisopropylamide, 2.83 mmol, was added to 1.0 g (2.79 mmol) of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ in 50 ml of THF at -78°C producing a green reaction mixture. After it had been stirred for 15 min at -78°C , 1.0 ml (8.69 mmol) of benzyl chloride (Aldrich) was added. The solution was removed from the cold bath and stirred for 3 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to column chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band

which yielded 0.70 g (1.55 mmol, 56% yield) of $(\mu\text{-SCHSCH}_2\text{Ph})\text{-Fe}_2(\text{CO})_6$ as an air-stable red solid, mp 116-118°C after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 1492(m), 1452(m), 691(m), 605(s), 585(s), 561(s), 550(s) cm^{-1} ;

terminal carbonyl region (pentane): 2070(s), 2024(vs), 2002(vs), 1992(s), 1979(m), 1974(m) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 3.82 (s, 1H, S_2CH), 3.79 (ABq, $J_{\text{AB}} = 13.1\text{Hz}$, 2H, SCH_2), 3.79 and 7.28 (both m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 52.4 (d, $J = 192\text{Hz}$, S_2CH), 57.8 (t, $J = 140\text{Hz}$, SCH_2), 128.5 (d, $J = 162\text{Hz}$, Ph), 129.1 (d, $J = 162\text{Hz}$, Ph), 133.6 (s, ipso Ph), 208.6 (br, CO) and 211.1 (s, CO).

Mass spectrum, m/z (relative intensity): 448 (M^+ , 1), 364 ($\text{M}^+ - 3\text{CO}$, 3), 357 ($\text{M}^+ - \text{PhCH}_2$, 59), 336 ($\text{M}^+ - 4\text{CO}$, 5), 329 ($\text{M}^+ - \text{PhCH}_2 - \text{CO}$, 10), 308 ($\text{M}^+ - 5\text{CO}$, 9), 301 ($\text{M}^+ - \text{PhCH}_2 - 2\text{CO}$, 7), 280 ($\text{M}^+ - 6\text{CO}$, 100), 273 ($\text{M}^+ - \text{PhCH}_2 - 3\text{CO}$, 2), 217 ($\text{M}^+ - \text{PhCH}_2 - 5\text{CO}$, 7), 189 ($\text{Fe}_2\text{S}_2\text{CH}$, 53), 188 ($\text{Fe}_2\text{S}_2\text{C}$, 24), 176 (Fe_2S_2 , 83), 144 (Fe_2S , 73), 112 (Fe_2 , 15), 91 (PhCH_2 , 47), 88 (FeS , 5), 56 (Fe, 21).

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2$: C, 37.53; H, 1.80%.

Found: C, 37.36; H, 1.92%.

Reaction Between (μ -Methanedithiolato)bis(tricarbonyliron), Lithium Diisopropylamide and Allyl Chloride. (GBW-VII-1).

Lithium diisopropylamide, 3.11 mmol, was added to 1.0 g (2.79 mmol) of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ in 50 ml of THF at -78°C

producing a green reaction mixture. After it had been stirred for 0.5 h, 2.0 ml (24.5 mmol) of allyl chloride (Aldrich) was added. The solution was removed from the cold bath and stirred for 2 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil was taken up in pentane/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to column chromatography (silicic acid/pentane). Pentane eluted a minor yellow band of $(\mu\text{-H}_2\text{CS}_2)\text{Fe}_2(\text{CO})_6$ and pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which yielded 0.776 g (1.95 mmol, 70% yield) of $(\mu\text{-SCHSCH}_2\text{CH=CH}_2)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil.

IR (CHCl_3): 1631(m), 1424(m), 1400(w), 1155(w), 1067(w), 984(s), 929(s), 605(s), 585(s), 561(s), 550(s) cm^{-1} ;

terminal carbonyl region (pentane): 2078(s), 2030(vs), 2007(vs), 1994(s), 1983(m), 1976(m) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 3.22 (d, $J = 7.35\text{Hz}$, 2H, SCH_2), 3.94 (s, 1H, S_2CH), 5.33 (d, 1H, $J = 16.4\text{Hz}$, vinyl), 5.34 (d, 1H, $J = 10.33\text{Hz}$, vinyl) and 5.71 (m, 1H, $-\text{CH=}$).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 52.0 (d, $J = 187\text{Hz}$, S_2CH), 55.2 (t, $J = 143\text{Hz}$, S-CH_2), 121.9 (t, $J = 159\text{Hz}$, $=\text{CH}_2$), 128.9 (d, $J = 158\text{Hz}$, $-\text{CH=}$), 208.5 (broad CO) and 211.2 (s, CO).

Mass spectrum, m/z (relative intensity): 398 (M^+ , 3), 370 ($\text{M}^+ - \text{CO}$, 3), 357 ($\text{M}^+ - \text{C}_3\text{H}_5$, 67), 342 ($\text{M}^+ - 2\text{CO}$, 6), 314 ($\text{M}^+ - 3\text{CO}$, 11), 329 ($\text{M}^+ - \text{C}_3\text{H}_5 - \text{CO}$, 15), 301 ($\text{M}^+ - \text{C}_3\text{H}_5 - 2\text{CO}$, 6), 286 ($\text{M}^+ - 4\text{CO}$, 14), 273 ($\text{M}^+ - \text{C}_3\text{H}_5 - 3\text{CO}$, 4), 258 ($\text{M}^+ - 5\text{CO}$, 45), 245 ($\text{M}^+ - \text{C}_3\text{H}_5 - 4\text{CO}$,

7), 230 ($M^+ - 6CO$, 100), 217 ($M^+ - C_3H_5 - 5CO$, 21), 189 (Fe_2S_2CH , 58), 188 (Fe_2S_2C , 25), 176 (Fe_2S_2 , 91), 144 (Fe_2S , 41), 112 (Fe_2 , 11), 56 (Fe , 17).

Anal. Calcd. for $C_{10}H_6Fe_2O_6S_2$: C, 30.18; H, 1.52%.

Found: C, 30.38; H, 1.60%.

Reaction Between Triiron Dodecacarbonyl and α,α -Toluenedithiol.
(GBW-X-71).

A 250 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 4.53 g (9.0 mmol) of $Fe_3(CO)_{12}$ and flushed with nitrogen. THF (50 ml) and 1.38 g (8.83 mmol) of α,α -toluenedithiol²³ were added by syringe and the mixture was gently refluxed for 1 h. The solvent was removed and the remaining red oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor dark red band which was not collected. Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which yielded 0.83 g (1.91 mmol, 22% yield) of $(\mu-PhHCS_2)Fe_2(CO)_6$ ²⁴ as an air-stable red solid, mp 93-94°C after crystallization from pentane.

IR ($CHCl_3$): 3065(w), 1603(w), 1496(m), 1448(m), 1230(br), 110(w), 1033(w), 1004(w), 847(m), 700(s), 620(s), 565(s), 488(m) cm^{-1} .

Terminal carbonyl region (pentane): 2084(s), 2043(vs), 2007(vs), 1988(m), 1958(w) cm^{-1} .

1H NMR (d_6 -acetone, 90MHz): δ 6.37 (s, 1H, CH) and 7.4 (m, 5H, Ph).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 79.1 (d, $J = 166\text{Hz}$, CH), 125.0 (d, $J = 160\text{Hz}$, Ph), 128.3 (d, $J = 162\text{Hz}$, Ph), 142.8 (s, ipso Ph), 208.0 and 208.4 (both s, CO).

Mass spectrum, m/z (relative intensity): 434 (M^+ , 7), 406 ($\text{M}^+ - \text{CO}$, 7), 378 ($\text{M}^+ - 2\text{CO}$, 9), 350 ($\text{M}^+ - 3\text{CO}$, 15), 322 ($\text{M}^+ - 4\text{CO}$, 8), 294 ($\text{M}^+ - 5\text{CO}$, 16), 266 ($\text{M}^+ - 6\text{CO}$, 100), 188 ($\text{Fe}_2\text{S}_2\text{C}$, 29), 176 (Fe_2S_2 , 11), 144 (Fe_2S , 44), 122 (Fe_2 , 5), 88 (FeS , 5), 56 (Fe , 14).

Anal. Calcd. for $\text{C}_{13}\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$: C, 35.98; H, 1.39%.

Found: C, 36.11; H, 1.47%.

Reaction Between $(\mu\text{-PhHCS}_2)\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodomethane. (GBW-X-41).

Lithium diisopropylamide, 0.90 mmol, was added to 0.36 g (0.83 mmol) of $(\mu\text{-PhHCS}_2)\text{Fe}_2(\text{CO})_6$ in 50 ml of THF at -78°C producing a green reaction mixture. After it had been stirred for 25 min at -78°C , 0.5 ml (8.0 mmol) of MeI (Aldrich) was added. The solution was removed from the cold bath and stirred for 1.5 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in pentane and applied to filtration chromatography (silicic acid). Pentane eluted a yellow band which yielded 0.06 g (0.14 mmol, 17% yield) of recovered starting material. Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which gave 0.29 g (0.65 mmol, 78% yield) of $(\mu\text{-SCPhSMe})\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp $101\text{-}102^\circ\text{C}$ after recrystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3000(w), 2960(w), 2925(w), 1595(m), 1492(m),

1444(m), 1416(w), 1304(m), 1264(w), 1074(w), 950(m), 903(m),
692(m), 639(s), 610(s), 590(s), 560(s) cm^{-1} ;

Terminal carbonyl region (pentane): 2070(s), 2028(vs), 2004(vs),
1994(s), 1982(m), 1973(m) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 2.13 (s, 3H, CH_3) and 7.2 (m, 5H, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 32.7 (CH_3), 73.7 (S_2C), 123.3, 127.4, 129.1 (Ph), 147.4 (ipso Ph) and 211.6 (br, CO).

Mass spectrum, m/z (relative intensity): 448 (M^+ , 8), 420 ($\text{M}^+ - \text{CO}$, 19), 392 ($\text{M}^+ - 2\text{CO}$, 43), 364 ($\text{M}^+ - 3\text{CO}$, 43), 336 ($\text{M}^+ - 4\text{CO}$, 36), 308 ($\text{M}^+ - 5\text{CO}$, 33), 280 ($\text{M}^+ - 6\text{CO}$, 100), 265 ($\text{Fe}_2\text{S}_2\text{CPh}$, 23), 176 (Fe_2S_2 , 97), 144 (Fe_2S , 33), 121 (PhCS, 16), 112 (Fe_2 , 5), 56 (Fe, 10).

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2$: C, 37.53; H, 1.80%.

Found: C, 37.53; H, 1.85%.

Reaction Between $(\mu\text{-PhHCS}_2)\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodoethane. (GBW-X-72).

Lithium diisopropylamide, 1.0 mmol, was added to 0.40 g (0.92 mmol) of $(\mu\text{-PhHCS}_2)\text{Fe}_2(\text{CO})_6$ in 50 ml of THF at -78°C producing a green reaction mixture. After it had been stirred for 30 min at -78°C , 0.75 ml (9.40 mmol) of iodoethane (Aldrich) was added. The solution was removed from the cold bath and stirred for 1 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil subjected to filtration chromatography (silicic acid/pentane).

Pentane eluted a yellow band which yielded 0.10 g (0.23 mmol, 25% yield) of recovered starting material. Further elution with pentane moved a red band which yielded 0.26 g (0.56 mmol, 61% yield) of $(\mu\text{-SCPhSEt})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil.

IR (pentane) (terminal carbonyl region): 2076(s), 2032(vs), 2008(vs), 1994(s), 1983(m), 1974(m) cm^{-1} .

^1H NMR (CD_2Cl_2 , 90MHz): δ 1.04 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 2.52 (m, 2H, SCH_2), 7.23 (s, 5H, Ph).

^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 22.5MHz): δ_{C} 11.7 (CH_3), 44.0 (SCH_2), 72.4 (S_2C), 123.4, 127.5, 129.1, 148.4 (Ph), 209.7 (broad, CO) and 211.6 (CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}_2$: C, 38.99; H, 2.18%.

Found: C, 39.04; H, 2.35%.

Reaction Between Cyclopentadienylirondicarbonyl Iodide and Lithium Dithioformate. (GBW-VIII-47).

A 100 ml, round-bottomed flask equipped with a stir-bar and serum cap was flushed with nitrogen and charged with 15 ml of THF and 0.4 ml (6.6 mmol) of CS_2 (MCB). To this solution was added 4.0 ml (4.0 mmol) of a 1M LiBEt_3H solution (Aldrich) and the resulting solution was stirred for 0.5 h. The dithioformate anion solution thus formed was cannulated into a solution of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ [1.22 g (4.0 mmol)] in 50 ml of THF and this mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure, leaving a red oil which was extracted with CH_2Cl_2 . The extracts were fil-

tered through a pad of silicic acid. After removal of the solvent, the residue was applied to a filtration chromatography funnel (silicic acid/pentane. Pentane/ CH_2Cl_2 (1/4, v/v) eluted an orange band which yielded 0.78 g (3.07 mmol, 77% yield) of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SC}(\text{S})\text{H}$ as a red-brown, air-stable solid, mp 61-63°C after crystallization from CH_2Cl_2 /pentane.

IR (CHCl_3): 3058(w), 2995(m), 1425(m), 1230(s), 1016(s), 841(m), 730(broad), 600(m), 567(m), 534(m) cm^{-1} ;

terminal carbonyl region (pentane): 2051(vs), 2010(vs) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 5.08 (s, 5H, C_5H_5 ring) and 11.27 (s, 1H, S_2CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 85.5 (d, $J = 183\text{Hz}$, C_5H_5), 210.5 (s, CO) and 233.1 (d, $J = 174\text{Hz}$, S_2CH).

Mass spectrum, m/z (relative intensity): 254 (M^+ , 2), 226 ($\text{M}^+ - \text{CO}$, 24), 198 ($\text{M}^+ - 2\text{CO}$, 43), 154 (CpFeSH , 9), 122 (CpFeH , 68), 121 (CpFe , 65), 56 (Fe, 100).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{FeO}_2\text{S}_2$: C, 37.81; H, 2.38%.

Found: C, 37.89; H, 2.48%.

Reaction Between Diiron Nonacarbonyl, Lithium Dithioformate and Iodomethane. (GBW-VIII-7).

A 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 3.3 g (9.0 mmol) of $\text{Fe}_2(\text{CO})_9$ and flushed with nitrogen. Subsequently, 50 ml of THF was added.

In a separate 100 ml, round-bottomed flask, 8 ml (8.0 mmol) of a 1M LiBEt_3H solution (Aldrich) was added dropwise

to 0.5 ml (8.0 mmol) of CS_2 (MCB) in 15 ml of THF. The reaction mixture immediately turned orange. It was stirred for 0.5 h, and then 1.0 ml (16.1 mmol) of MeI (Aldrich) was added. The resulting solution was cannulated into the $\text{Fe}_2(\text{CO})_9/\text{THF}$ solution, and the reaction mixture was refluxed gently for 1 h. Subsequently, the solvent was removed under reduced pressure, leaving a brown tar which was extracted with pentane/ CH_2Cl_2 (4/1, v/v). The extracts were filtered through a pad of silicic acid. After removal of the solvent, the red oil which remained was applied to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted a orange band which yielded 0.90 g (2.42 mmol, 30% yield based on CS_2) of $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified by comparison of its ^1H NMR and IR spectra to those of an authentic sample.

Reaction Between Diiron Nonacarbonyl, Lithium Dithioformate and Iodoethane. (GBW-IX-60).

Following the procedure outlined on p.241, a 15 ml THF solution of 8.0 mmol of lithium dithioformate (8.0 mmol each of LiBEt_3H and CS_2) and 1.29 ml (16.1 mmol) of iodoethane (Aldrich) was cannulated into a 50 ml THF solution of $\text{Fe}_2(\text{CO})_9$. The reaction mixture was refluxed gently for 1 h. Subsequently, the solvent was removed under reduced pressure leaving a red oil which was extracted with pentane/ CH_2Cl_2 (4/1, v/v). The extracts were filtered through a pad of silicic acid. After removal of the solvent, the red oil which remained was subjected to filtration chromatography (silicic acid/pentane).

Pentane/CH₂Cl₂ (9/1, v/v) eluted a red band which yielded 0.94 g (2.44 mmol, 30% yield based on CS₂) of (μ-SCHSEt)Fe₂(CO)₆ as a slightly air-sensitive red oil identified by comparison of its ¹H NMR and IR spectra to those of an authentic sample.

Reaction Between Diiron Nonacarbonyl, Lithium Dithioformate and Allyl Chloride. (GBW-IX-63).

Following the procedure outlines on p.243, a 15 ml THF solution of 8.0 mmol of lithium dithioformate (8.0 mmol each of LiBEt₃H and CS₂) and 1.3 ml (16.1 mmol) of allyl chloride (Aldrich) was cannulated into a 50 ml THF solution of Fe₂(CO)₉. The reaction mixture was refluxed gently for 1 h. Subsequently, the solvent was removed under reduced pressure leaving a brown tar which was extracted with pentane/CH₂Cl₂ (4/1, v/v). The extracts were filtered through a pad of silicic acid. After removal of the solvent, the red oil which remained was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band yielding 0.127 g (0.30 mmol, 7% yield based on CS₂) of (μ-CH₂=CHCH₂S)₂Fe₂(CO)₆ as a red oil identified by comparison of its ¹H NMR spectrum to that of an authentic sample.¹¹ Pentane/CH₂Cl₂ (9/1, v/v) eluted an orange band which yielded 0.374 g (0.94 mmol, 12% yield based on CS₂) of (μ-SCHSCH₂CH=CH₂)Fe₂(CO)₆ as a slightly air-sensitive red oil identified by comparison of its ¹H NMR and Mass spectra to those of an authentic sample.

Reaction Between $(\mu\text{-SCHSMe})\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodomethane. (GBW-VII-34).

A 250 ml round-bottomed flask containing 0.624 g (1.68 mmol) of $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$ was equipped with a stir-bar and a serum cap and flushed with nitrogen. THF (50 ml) was added and the red solution cooled to -78°C . Lithium diisopropylamide (1.90 mmol) in 15 ml of THF then was cannulated into the solution which became red-brown. The reaction mixture was stirred for 45 min, then 1.0 ml (16.1 mmol) of iodomethane (Aldrich) was added. The reaction vessel was removed from the cold bath and the solution was stirred for 22 h. The solvent was removed and the residue taken up in CH_2Cl_2 and filtered through a pad of silicic acid. The solvent was again removed leaving an orange solid which was subjected to column chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a minor orange band which yielded 0.11 g (0.30 mmol, 11% yield) of $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$ identified by comparison of its ^1H NMR spectrum to that of an authentic sample. Further elution with pentane/ CH_2Cl_2 (1/1, v/v) moved an orange band which yielded 0.50 g (1.30 mmol, 77% yield) of $(\mu\text{-SCSMe}_2)\text{Fe}_2(\text{CO})_6$ as an air-stable orange solid. After recrystallization from pentane/ CH_2Cl_2 , mp 130°C dec, it was identified based on the following data:

IR (CH_2Cl_2) (terminal carbonyl region): 2047(s), 2003(vs), 1975(vs), 1954(s) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 2.80 (s, CH_3).

^{13}C NMR (d_6 -acetone, 67.9MHz): δ_{C} 33.2 (q, $J = 144\text{Hz}$, CH_3), 106.7 (s, S_2C), 214.0 (s, CO).

Mass spectrum, m/z (relative intensity): 386 (M^+ , 1), 358 ($\text{M}^+ - \text{CO}$, <1), 274 ($\text{M}^+ - 4\text{CO}$, 1), 246 ($\text{M}^+ - 5\text{CO}$, 2), 212 ($\text{M}^+ - 4\text{CO} - \text{Me}_2\text{S}$, 1), 184 ($\text{M}^+ - 5\text{CO} - \text{Me}_2\text{S}$, 1), 176 (Fe_2S_2 , 3), 156 (Fe_2SC , 3), 144 (Fe_2S , 1), 112 (Fe_2S , 5), 100 (FeSC , 3), 76 (CS_2 , 3), 62 (Me_2S , 75), 47 (SMe , 100).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$: C, 28.01; H, 1.57%.

Found: C, 28.02; H, 1.67%.

Reaction Between $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Allyl Bromide. (GBW-VII-25).

In 50 ml of THF, 0.37 g (0.99 mmol) of $(\mu\text{-SCHSCH}_3)\text{Fe}_2(\text{CO})_6$ was cooled to -78°C and 1.30 mmol of LDA in 15 ml of THF was added to the solution. The reaction mixture became red-brown and was stirred for 30 min before 1.0 ml (11.56 mmol) of allyl bromide (Anachemia) was added. The reaction mixture was removed from the cold bath and stirred for 3.5 h. The reaction mixture was filtered through a pad of silicic acid and the solvent removed. The brown oil which remained was subjected to column chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a minor orange band which was not collected. Further elution with pentane/ CH_2Cl_2 (1/1, v/v) moved an orange band which yielded 0.16 g (0.39 mmol, 39% yield) of $[\mu\text{-SCSMe}(\text{CH}_2\text{CH}=\text{CH}_2)]\text{Fe}_2(\text{CO})_6$ as an air-stable orange solid. After crystallization from pentane/ CH_2Cl_2 , mp $81\text{-}83^\circ\text{C}$, it was identified based on the following data:

IR (CH_2Cl_2) (terminal carbonyl region): 2050(s), 2005(s), 1974(s), 1953(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 2.73 (s, 3H, S- CH_3), 3.55 (dd, $J = 12.8$, $J = 10.7\text{Hz}$, 1H, allylic proton), 3.90 (dd, $J = 12.8\text{Hz}$, $J = 9.6\text{Hz}$, 1H, allylic proton), 5.60 (d, $J = 17.3\text{Hz}$, 1H, vinyl), 5.65 (d, $J = 9.9\text{Hz}$, 1H, vinyl) and 5.84 (m, 1H, $\text{CH}_2\text{CH=}$).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 29.7 (q, $J = 144\text{Hz}$, CH_3), 53.7 (t, $J = 146\text{Hz}$, SCH_2), 101.5 (s, SCS), 124.3 (d, $J = 166\text{Hz}$, CH=), 126.9 (t, $J = 162\text{Hz}$, $=\text{CH}_2$) and 212.9 (s, CO).

Mass spectrum, m/z (relative intensity): 412 (M^+ , 14), 384 ($\text{M}^+ - \text{CO}$, 3), 371 ($\text{M}^+ - \text{C}_3\text{H}_5$, 5), 356 ($\text{M}^+ - 2\text{CO}$, 5), 343 ($\text{M}^+ - \text{CO} - \text{C}_3\text{H}_5$, 1), 328 ($\text{M}^+ - 3\text{CO}$, 11), 315, ($\text{M}^+ - 2\text{CO} - \text{C}_3\text{H}_5$, 4), 300 ($\text{M}^+ - 4\text{CO}$, 9), 287 ($\text{M}^+ - 3\text{CO} - \text{C}_3\text{H}_5$, 4), 272 ($\text{M}^+ - 5\text{CO}$, 23), 259 ($\text{M}^+ - 4\text{CO} - \text{C}_3\text{H}_5$, 7), 244 ($\text{M}^+ - 6\text{CO}$, 31), 240 ($\text{M}^+ - 3\text{CO} - \text{SMe}(\text{C}_3\text{H}_5)$, 6), 231 ($\text{M}^+ - 5\text{CO} - \text{C}_3\text{H}_5$, 7), 212 ($\text{M}^+ - 4\text{CO} - \text{SMe}(\text{C}_3\text{H}_5)$, 10), 203 ($\text{M}^+ - 6\text{CO} - \text{C}_3\text{H}_5$, 14), 188 ($\text{Fe}_2 - \text{S}_2\text{C}$, 26), 184 ($\text{M}^+ - 5\text{CO} - \text{SMe}(\text{C}_3\text{H}_5)$, 15), 176 (Fe_2S_2 , 100), 156 (Fe_2SC , 21), 144 (Fe_2S , 47), 112 (Fe_2 , 29), 100 (FeSC , 14), 88 (FeS , 8), 56 (Fe, 41).

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_2$: C, 32.07; H, 1.96%.

Found: C, 32.12; H, 2.02%.

Reaction Between $(\mu\text{-SCHSEt})\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodomethane. (GBW-VI-60).

In 50 ml of THF, 0.48 g (1.24 mmol) of $(\mu\text{-SCHSEt})\text{Fe}_2(\text{CO})_6$ was cooled to -78°C and 1.30 mmol of LDA in 15 ml of THF was added to the solution. The reaction mixture became red-brown and was stirred for 30 min before 1.5 ml (24 mmol) of

iodomethane (Aldrich) was added. The reaction mixture was removed from the cold bath and stirred for 5 h. The solvent was removed and the remaining red oil was dissolved in CH_2Cl_2 and filtered through a pad of silicic acid. After removal of solvent, the red oil was subjected to column chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a minor brown band which was not collected. Further elution with pentane/ CH_2Cl_2 (1/1, v/v) moved an orange band which yielded 0.42 g (1.04 mmol, 84% yield) of $(\mu\text{-SCSMe(Et)})\text{Fe}_2(\text{CO})_6$ as an air-stable, orange solid. After crystallization from pentane/ CH_2Cl_2 , mp 73-75°C, it was identified based on the following data:

IR (CH_2Cl_2) (terminal carbonyl region): 2048(s), 2005(vs), 1973(vs), 1954(s) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 1.49 (t, $J = 7.8\text{Hz}$, 3H, CH_3), 2.73 (s, 3H, SCH_3), 3.07 (q, $J = 7.8\text{Hz}$, 2H, CH_2).

^{13}C NMR (CDCl_3 , 22.5MHz): δ_{C} 9.2 (q, $J = 130\text{Hz}$, CH_3), 29.8 (q, $J = 144\text{Hz}$, SCH_3), 44.7 (t, $J = 143\text{Hz}$, CH_2), 102.1 (s, S_2C) and 212.8 (s, CO).

Mass spectrum, m/z (relative intensity): 400 (M^+ , 34), 372 ($\text{M}^+ - \text{CO}$, 19), 344 ($\text{M}^+ - 2\text{CO}$, 16), 316 ($\text{M}^+ - 3\text{CO}$, 16), 288 ($\text{M}^+ - 4\text{CO}$, 32), 260 ($\text{M}^+ - 5\text{CO}$, 75), 240 ($\text{M}^+ - 3\text{CO} - \text{SMe(Et)}$, 19), 232 ($\text{M}^+ - 6\text{CO}$, 24), 212 ($\text{M}^+ - 4\text{CO} - \text{SMe(Et)}$, 23), 204 ($\text{Fe}_2\text{S}_2\text{C}_2\text{H}_4$, 14), 184 ($\text{M}^+ - 5\text{CO} - \text{SMe(Et)}$, 28), 176 (Fe_2S_2 , 100), 156 (Fe_2SC , 51), 144 (Fe_2S , 54), 112 (Fe_2 , 51), 100 (FeSC , 27), 88 (FeS , 10), 76 (SMe(Et) , 54), 61 (SEt , 74), 56 (Fe , 56), 47 (SMe , 39).

Anal. Calcd. for $C_{10}H_8Fe_2O_6S_2$: C, 30.03; H, 2.02%.

Found: C, 30.11; H, 2.03%.

Reaction Between $(\mu-SCHSEt)Fe_2(CO)_6$, Lithium Diisopropylamide and Iodoethane. (GBW-XI-3).

In 50 ml of THF, 0.74 g (1.92 mmol) of $(\mu-SCHSEt)Fe_2(CO)_6$ was cooled to $-78^\circ C$ and 2.45 mmol of LDA in 15 ml of THF was added to the solution. The reaction mixture became red-brown and was stirred for 30 min before 1.0 ml (12.5 mmol) of iodo-methane (Aldrich) was added. The reaction mixture was removed from the cold bath and stirred for 24 h. The solvent was removed and the remaining red oil was dissolved in CH_2Cl_2 /pentane (1/1, v/v) and filtered through a pad of silicic acid. After removal of the solvent, the red oil was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted a minor brown band which was not collected. Further elution with pentane/ CH_2Cl_2 (1/1, v/v) moved an orange band which yielded 0.36 g (0.87 mmol, 45% yield) of $(\mu-SCSEt)_2-Fe_2(CO)_6$ as an air-stable; orange solid, mp $75-77^\circ C$ after crystallization from pentane/ CH_2Cl_2 .

IR (CH_2Cl_2) (terminal carbonyl region): 2057(s), 2009(vs), 1973(vs), 1954(s) cm^{-1} .

1H NMR ($CDCl_3$, 250MHz): δ 1.51 (t, J = 7.5Hz, CH_3) and 3.07 (m, 2H, SCH_2).

^{13}C NMR ($CDCl_3$, 67.9MHz): δ_C 9.6 (q, J = 130Hz, CH_3), 42.2 (t, J = 144Hz, SCH_2), 99.9 (s, CS_2) and 212.9 (s, CO).

Anal. Calcd. for $C_{11}H_{10}Fe_2O_6S_2$: C, 31.91; H, 2.43%.

Found: C, 32.11; H, 2.45%.

Reaction Between Diiron Nonacarbonyl and O-Ethyl Thioacetate.
(GBW-VIII-10).

A 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 3.0 g (8.25 mmol) of $Fe_2(CO)_9$ and flushed with nitrogen. Toluene (50 ml) and 0.73 g (7.0 mmol) of O-ethyl thioacetate were added by syringe, and the reaction mixture was heated to 70°C in an oil bath for 30 min. Subsequently, the solvent was removed and the red oil which remained was taken up in pentane and filtered through a pad of silicic acid. The solvent was again removed and the red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band which was not collected. Further elution with pentane moved a second orange-red band which after removal of solvent, yielded 0.80 g (2.08 mmol, 30% yield based on the thioester) of $(\mu-SC(Me)OEt)Fe_2(CO)_6$ as a black-red, slightly air-sensitive solid. After crystallization from pentane, mp 53-54°C, it was identified based on the following data:

IR ($CHCl_3$): 2987(m), 2912(m), 1463(w), 1442(m), 1387(s), 1371(m), 1359(m), 1168(m), 1096(w), 1067(s), 1021(s), 1010(s), 913(s), 896(s), 823(w), 725(s), 628(w), 613(w), 608(s), 580(s), 552(s) cm^{-1} ;

terminal carbonyl region (pentane): 2074(s), 2026(vs), 2003(s), 1997(vs), 1981(s), 1969(vs), 1957(s) cm^{-1} .

^1H NMR (CDCl_3): δ 0.87 (t, $J = 7.1\text{Hz}$, CH_3 of Et), 1.76 (s, 3H, CH_3) and 3.02 (m, 2H, CH_2).

^{13}C NMR (CDCl_3): δ_{C} 12.4 (q, $J = 128\text{Hz}$, CH_3), 33.9 (q, $J = 128\text{Hz}$, CH_3), 71.3 (t, $J = 146\text{Hz}$, OCH_2), 122.7 (s, S-C-O), 212.1 and 208.9 (both broad, $\text{Fe}(\text{CO})$).

FD mass spectrum: $M^+ = 384$ (calcd. M^+ : 383.93).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{Fe}_2\text{O}_7\text{S}$: C, 31.28; H, 2.10%.

Found: C, 31.21; H, 2.14%.

Reaction Between Diiron Nonacarbonyl and O-Ethyl Thiopropanoate.
(GBW-VIII-11).

In 50 ml of toluene, 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and 0.83 g (7.0 mmol) of O-ethyl thiopropanoate were stirred at 70°C for 30 min. The solvent was removed and the red oil which remained was taken up in pentane and filtered through a pad of silicic acid. The solvent was again removed and the red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band of $\text{S}_2\text{Fe}_3(\text{CO})_9$. Further elution with pentane/ CH_2Cl_2 (9/1, v/v) moved an orange-red band which yielded 0.84 g (2.11 mmol, 30% yield based on the thioester) of $(\mu\text{-SC}(\text{Et})\text{OEt})\text{Fe}_2(\text{CO})_6$ as a black-red, slightly air-sensitive solid. After crystallization from pentane, mp $67.5\text{-}68.5^\circ\text{C}$, it was identified based on the following data:

IR (CHCl_3): 2976(m), 2941(w), 1445(m), 1385(m), 1254(w), 1207(m), 1160(m), 1142(w), 1098(m), 1066(m), 1021(m), 1010(m), 907(m), 830(w), 721(m), 662(m), 621(m), 584(s), 554(s) cm^{-1} ;

terminal carbonyl region (pentane): 2072(vs), 2025(vs), 2003(s), 1995(vs), 1978(s), 1967(s), 1956(s) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 0.89 (t, $J = 7.1\text{Hz}$, 6H, CH_3), 1.55, 2.20, 2.83 and 3.18 (all m, 4H, methylene protons).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 12.2 (q, $J = 127\text{Hz}$, CH_3), 39.2 (t, $J = 130\text{Hz}$, CH_2), 71.5 (t, $J = 145\text{Hz}$, OCH_2), 128.8 (s, $\text{S}-\underline{\text{C}}-\text{O}$), 212.1 and 209.0 (both broad, $\text{Fe}(\text{CO})$).

FD mass spectrum: $M^+ = 398$ (calcd. $M^+ = 397.95$).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_7\text{S}$: C, 33.20; H, 2.53%.

Found: C, 33.33; H, 2.60%.

Reaction Between O-Ethyl Thioformate and Diiron Nonacarbonyl.

(GBW-VII-14).

A 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and flushed with nitrogen. Toluene (50 ml) and 0.45 g (5.0 mmol) of O-ethyl thioformate were added by syringe. The reaction mixture was stirred in an oil bath at 70°C for 3 h. Subsequently, the solvent was removed under reduced pressure, leaving a red oil solid which was dissolved in pentane and filtered. The filtrate was concentrated and cooled to -20°C . The crystals which formed were collected, washed with a small amount of pentane and dried to yield 0.62 g (1.35 mmol, 54% yield based on $\text{HC}(\text{S})\text{OEt}$) of $([\mu\text{-SCH}(\text{OEt})]_2\text{Fe}_2(\text{CO})_6$ as a red-brown, air-stable solid, mp $\sim 100^\circ\text{C}$ dec . .

IR (CHCl_3): 2985(s), 2940(m), 2890(m), 1471(w), 1445(m), 1391(m), 1290(m), 1206(w), 1166(m), 1115(sh), 1085(vs), 1024(m), 960(m), 938(m), 865(m), 816(w), 725(m), 615(s), 585(s), 560(s) cm^{-1} ;

terminal carbonyl region (pentane): 2059(s), 2011(s), 1988(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.31 (t, $J = 7.0\text{Hz}$, 3H, CH_3), 4.05 (m, 2H, OCH_2 ; collapses to AX quartet [δ 4.13 and 3.96] $J_{\text{AX}} = 9.2\text{Hz}$), 7.18 (s, 1H, CH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 14.8 (q, $J = 127\text{Hz}$, CH_3), 72.5 (t, $J = 141\text{Hz}$, OCH_2), 114.3 (d, $J = 187\text{Hz}$, CH), 202.0, 207.9, 210.1 (all s, CO).

FD mass spectrum: $M^+ = 460$ (calcd. $M^+ = 460.04$).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{Fe}_2\text{O}_8\text{S}_2$: C, 31.33; H, 2.63%.

Found: C, 31.53; H, 2.68%.

Reaction Between $[\mu\text{-SCH}(\text{OEt})]_2\text{Fe}_2(\text{CO})_6$, Lithium Diisopropylamide and Iodomethane. (GBW-XI-22).

A 300 ml, round-bottomed flask equipped with a magnetic stir-bar and a serum cap was charged with 0.30 g (0.65 mmol) of $[\mu\text{-SCH}(\text{OEt})]_2\text{Fe}_2(\text{CO})_6$ and flushed with nitrogen. THF (50 ml) was added and the red solution cooled to -78°C . Lithium diisopropylamide (0.65 mmol) in 10 ml of THF was added and the solution became brown. The reaction mixture was stirred for 30 min then 0.5 ml (8.0 mmol) of iodomethane (Aldrich) was added. The mixture was stirred for another 30 min at -78°C

then removed from the cold bath and stirred for 18 h. The solvent was removed from the brown mixture leaving a black residue which was extracted with pentane/ CH_2Cl_2 (4/1, v/v). However, no tractable materials could be obtained after filtration through a pad of silicic acid.

Reaction Between Diiron Nonacarbonyl and S-Ethyl Thioacetate.
(GBW-IX-17).

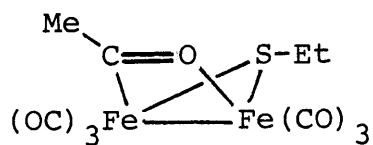
A 300 ml, three-necked, round-bottomed flask equipped with serum caps and a magnetic stir-bar was charged with 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and flushed with nitrogen. Toluene (60 ml) and 0.63 g (6.0 mmol) of S-ethyl thioacetate were added by syringe, and the reaction mixture was stirred for 48 h. Subsequently, the solvent was removed and the brown oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor orange band which was not collected. Further elution with pentane/ CH_2Cl_2 (9/1, v/v) moved two dark red bands. The first red band yielded 0.30 g (0.78 mmol, 13% yield based on the thioester) of $(\mu\text{-MeCO})\text{-}(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified as a 3.6/1 (e/a) mixture of two isomers.

IR (CHCl_3): 2992(w), 2975(m), 2938(m), 2878(w), 1512(s) (acyl CO), 1458(m), 1437(w), 1407(m), 1383(w), 1349(m), 1261(m), 1115(s), 1051(w), 979(m), 957(m), 616(s), 581(s) cm^{-1} ;

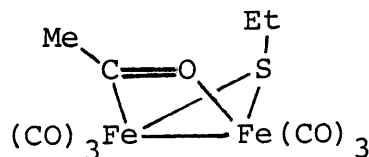
terminal carbonyl region (pentane): 2081(s), 2039(vs), 2009(s), 1997(s), 1972(s) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 1.37 (t, $J = 7.3\text{Hz}$, CH_3 , 42b),

1.48 (t, $J = 7.3\text{Hz}$, CH_3 , 42a), 2.25 (s, CH_3 , 42a), 2.31 (s, CH_3 , 42b) and 2.57 (m, SCH_2).



42a



42b

Isomer ratio 42a:42b = 3.6:1.

^{13}C NMR (CDCl_3 , 6719MHz): δ_{C} 17.9 (q, $J = 125\text{Hz}$, CH_2CH_3 , 42b), 18.4 (q, $J = 128\text{Hz}$, CH_2CH_3 , 42a), 26.0 (t, $J = 141\text{Hz}$, SCH_2 , 42b), 33.0 (t, $J = 141\text{Hz}$, SCH_2 , 42a), 46.8 (q, $J = 129\text{Hz}$, CH_3 , 42a), 47.2 (q, $J = 129\text{Hz}$, CH_3 , 42b), 207.7, 209.7, 209.9, 211.4, 212.1, (all s, CO), 299.2 (s, acyl CO, 42a) and 301.9 (s, acyl CO, 42b).

Mass spectrum, m/z (relative intensity): 384 (M^+ , 3), 356 ($\text{M}^+ - \text{CO}$, 10), 328 ($\text{M}^+ - 2\text{CO}$, 14), 300 ($\text{M}^+ - 3\text{CO}$, 17), 272 ($\text{M}^+ - 4\text{CO}$, 14), 244 ($\text{M}^+ - 5\text{CO}$, 30), 216 ($\text{M}^+ - 6\text{CO}$, 58), 188 ($\text{M}^+ - 7\text{CO}$, 19), 173 ($\text{Fe}_2\text{SC}_2\text{H}_5$, 15), 159 (Fe_2SCH_3 , 15), 144 (Fe_2S , 100), 112 (Fe_2 , 11), 88 (FeS , 7), 71 (FeCH_3 , 7), 56 (Fe , 38).

Anal. calcd. for $\text{C}_{10}\text{H}_8\text{Fe}_2\text{O}_7\text{S}$: C, 31.28; H, 2.10%.

Found: C, 31.30; H, 2.20%.

The second red band yielded 0.30 g (0.57 mmol, 10% yield based on thioester) of $(\mu_3\text{-EtS})(\mu_2\text{-MeCO})\text{Fe}_3(\text{CO})_9$ as a slightly air-sensitive, red-black solid. After recrystallization from CH_2Cl_2 /pentane, mp 90-92°C, it was identified based on the following data:

IR (CHCl_3): 2935(w), 1497(s) (acyl CO), 1454(m), 1422(w), 1380(w), 1347(m), 1254(w), 1093(s), 970(m), 647(m), 620(s), 607(s), 593(s), 555(s), 474(m) cm^{-1} ;

terminal carbonyl region (pentane): 2081(s), 2044(vs), 2020(vs), 2000(vs), 1994(sh), 1978(s), 1961(s), 1954(m) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 1.77 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 2.22 (s, 3H, CH_3) and 3.63 (q, $J = 7.3\text{Hz}$, 2H, SCH_2).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 17.5 (q, $J = 128\text{Hz}$, CH_2CH_3), 41.4 (t, $J = 145\text{Hz}$, SCH_2), 48.3 (q, $J = 127\text{Hz}$, CH_3), 202.4, 206.2, 207.2, 209.0, 213.6, 214.7, 216.3 (all s, CO) and 317.5 (s, acyl CO).

Mass spectrum, m/z (relative intensity): 496 ($\text{M}^+ - \text{CO}$, 3), 468 ($\text{M}^+ - 2\text{CO}$, 5), 440 ($\text{M}^+ - 3\text{CO}$, 2), 412 ($\text{M}^+ - 4\text{CO}$, 2), 384 ($\text{M}^+ - 5\text{CO}$, 12), 356 ($\text{M}^+ - 6\text{CO}$, 20), 328 ($\text{M}^+ - 7\text{CO}$, 25), 300 ($\text{M}^+ - 8\text{CO}$, 28), 272 ($\text{M}^+ - 9\text{CO}$, 20), 257 ($\text{Fe}_3\text{CO}(\text{SEt})$, 3), 244 ($\text{Fe}_3\text{Me}(\text{SEt})$, 33), 229 (Fe_3SEt , 7), 216 ($\text{Fe}_2(\text{OCMe})\text{SEt}$, 30), 200 (Fe_3S , 56), 188 ($\text{Fe}_2\text{SEt}(\text{Me})$, 14), 173 (Fe_2SEt , 12), 168 (Fe_3 , 5), 144 (Fe_2S , 100), 112 (Fe_2 , 15), 56 (Fe, 87).

Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{Fe}_3\text{O}_{10}\text{S}$: C, 29.81; H, 1.54%.

Found: C, 29.90; H, 1.61%.

Reaction Between Diiron Nonacarbonyl and S-Ethyl Thiobenzoate.
(GBW-IX-20).

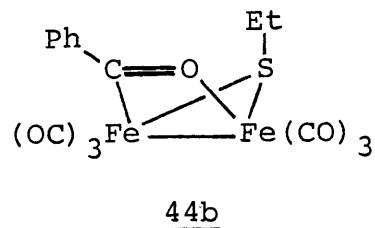
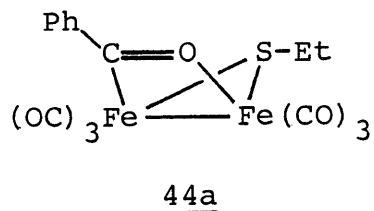
In 50 ml of toluene, 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and 1.0 g (6.0 mmol) of S-ethyl thiobenzoate were stirred for 48 h. Removal of the solvent left a brown oil which was subjected to

filtration chromatography (silicic acid/pet ether). Pet ether eluted a minor yellow band which was not collected. Pet ether- CH_2Cl_2 (9/1, v/v) eluted an orange band which yielded 0.44 g (1.0 mmol, 17% yield based on the thioester) of $(\mu\text{-EtS})(\mu\text{-PhCO})\text{-Fe}_2(\text{CO})_6$ as an air-stable red solid. After recrystallization from pentane, mp 81-86°C, it was identified on the basis of the following data:

IR (CHCl_3): 2993(w), 2970(w), 2938(w), 2878(w), 1597(w), 1470(s) (acyl CO), 1440(m), 1381(w), 1362(w), 1262(w), 1176(m), 1004(w), 978(w), 896(s), 693(m), 661(m), 628(m), 611(s), 585(s) cm^{-1} .

Terminal carbonyl region (pentane): 2069(s), 2019(vs), 2010(s), 1997(s), 1972(s) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 1.29 (t, $J = 7.3\text{Hz}$, CH_3 , 44b), 1.50 (t, $J = 7.3\text{Hz}$, CH_3 , 44a), 2.09, 2.29 (both m, CH_2 , 44b), 2.64 (m, CH_2 , 44a) and 7.5-7.3 (m, Ph).



Isomer ratio 44a:44b = 4.4:1.

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 17.8 (q, $J = 128\text{Hz}$, CH_3 , 44b), 18.3 (q, $J = 127\text{Hz}$, CH_3 , 44a), 26.0 (t, $J = 144\text{Hz}$, SCH_2 , 44b), 33.0 (t, $J = 141\text{Hz}$, SCH_2 , 44a), 126.8 (d, $J = 163\text{Hz}$, Ph), 127.2 (d, $J = 163\text{Hz}$, Ph), 128.3 (d, $J = 163\text{Hz}$, Ph), 128.6

(d, $J = 162\text{Hz}$, Ph), 133.4 (d, $J = 160\text{Hz}$, Ph), 144.5 (s, ipso Ph, 44a), 144.8 (s, ipso Ph, 44b), 207.7, 209.5, 209.9, 210.3, 211.3, 212.0 (all s, CO), 289.0 (s, acyl CO, 44a), 291.6 (s, acyl CO, 44b).

Mass spectrum, m/z (relative intensity): 446 (M^+ , 2), 418 ($M^+ - \text{CO}$, 2), 390 ($M^+ - 2\text{CO}$, 7), 362 ($M^+ - 3\text{CO}$, 16), 334 ($M^+ - 4\text{CO}$, 4), 306 ($M^+ - 5\text{CO}$, 15), 278 ($M^+ - 6\text{CO}$, 25), 250 ($\text{Fe}_2\text{SEt(Ph)}$, 33), 221 (Fe_2SPh , 28), 173 (Fe_2SEt , 6), 165 (FeSPh , 10), 144 (Fe_2S , 100), 112 (Fe_2 , 9), 105 (PhCO , 9), 77 (Ph, 18), 56 (Fe, 37).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{Fe}_2\text{O}_7\text{S}$: C, 40.40; H, 2.26%.

Found: C, 40.33; H, 2.29%.

Reaction Between Diiron Nonacarbonyl and S-Ethyl Thiopivalate.
(GBW-IX-26).

In 50 ml of toluene, 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and 0.88 g (6.0 mmol) of S-ethyl thiopivalate were stirred for 48 h. Removal of the solvent left a red tar which was subjected to filtration chromatography (silicic acid/pet ether). Pet ether eluted an orange band which yielded 0.26 g (0.63 mmol, 10% yield based on thioester) of $(\mu\text{-EtS})(\mu\text{-Me}_3\text{CCO})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After crystallization from pentane, mp $36\text{-}38^\circ\text{C}$, it was identified as one isomer (e, Et) by its ^1H NMR spectrum.

IR (CHCl_3): 2975(m), 2939(m), 2910(w), 2879(w), 1496(s) (acyl CO), 1479(sh), 1463(m), 1438(w), 1395(w), 1382(w), 1367(m), 1262(m), 1038(w), 978(w), 924(s), 692(w), 673(w), 615(s), 580(s) cm^{-1} ;

terminal carbonyl region (pentane): 2082(s), 2040(vs), 2010(s), 1995(s), 1970(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.86 (s, 9H, *t*-butyl), 1.48 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 2.58 (m, 2H, SCH_2).

Mass spectrum, m/z (relative intensity): 426 (M^+ , 11), 398 ($\text{M}^+ - \text{CO}$, 7), 370 ($\text{M}^+ - 2\text{CO}$, 13), 342 ($\text{M}^+ - 3\text{CO}$, 40), 314 ($\text{M}^+ - 4\text{CO}$, 32), 286 ($\text{M}^+ - 5\text{CO}$, 43), 258 ($\text{M}^+ - 6\text{CO}$, 100), 230 ($\text{M}^+ - 7\text{CO}$, 31), 200 ($\text{Fe}_2\text{SC}_4\text{H}_8$, 54), 175 (Fe_2SEt , 20), 144 (Fe_2S , 60), 57 (C_4H_9 , 19), 56 (Fe, 11).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{Fe}_2\text{O}_7\text{S}$: C, 36.65; H, 3.31%.

Found: C, 36.98; H, 3.40%.

Reaction Between Diiron Nonacarbonyl and S-Ethyl Thioformate.
(GBW-IX-14).

A 300 ml, three-necked, round-bottomed flask equipped with serum caps and a magnetic stir-bar was charged with 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and flushed with nitrogen. Toluene (50 ml) and 0.61 g (6.77 mmol) of S-ethyl thioformate were added by syringe, and the reaction mixture was stirred for 17 h at room temperature. After this time, TLC (silicic gel, J.T. Baker/pentane) analysis of the solution showed no product formation so the mixture was heated in an oil bath at 70°C . After 1 h the solvent was removed from the red solution, leaving a red residue which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands, the first yielding 0.20 g (0.50 mmol, 15% yield based on HC(O)SEt) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ (e,a isomer) mp $75\text{--}77^\circ\text{C}$ (lit.⁵⁶

mp 75-76°C); the second band gave 0.11 g (0.154 mmol, 9% yield based on HC(O)SEt) of $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]_2\text{S}$ (e,e) as a dark red, air-stable solid, mp 154-156°C (dec) after crystallization from pentane.

IR (pentane) (terminal carbonyl region): 2087(m), 2058(s), 2045(vs), 2011(s), 1998(vs), 1982(w) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.37 (t, $J = 7.4\text{Hz}$, 2H, CH_3), 2.44 (m, 2H, SCH_2).

Mass spectrum, m/z (relative intensity): 657 (M^+-2CO , 10), 630 (M^+-3CO , 4), 602 (M^+-4CO , 10), 574 (M^+-5CO , 5), 546 (M^+-6CO , 4), 518 (M^+-7CO , 8), 490 (M^+-8CO , 20), 462 (M^+-9CO , 31), 434 (M^+-10CO , 3), 406 (M^+-11CO , 19), 320 (Fe_4S_3 , 100), 264 (Fe_3S_3 , 22), 232 (Fe_3S_2 , 13), 176 (Fe_2S_2 , 14), 144 (Fe_2S , 11).

Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_3$: C, 26.92; H, 1.41%.

Found: C, 26.82; H, 1.45%.

Reaction Between Triiron Dodecacarbonyl and S-Ethyl Thioacetate. (GBW-IX-24).

A 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar, serum caps and a reflux condenser was charged with 3.0 g (5.96 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and flushed with nitrogen. Toluene (75 ml) and 0.63 g (6.0 mmol) of S-ethyl thioacetate were added by syringe, and the reaction mixture was stirred at room temperature for 24 h. Analysis of the solution by TLC (eluting with pentane) indicated no

product formation. Therefore, the reaction vessel was placed in an oil bath at 75°C, and the reaction mixture was stirred for 22.5 h. The solvent was removed from the now dark red solution, leaving a red oil which was subjected to filtration chromatography (silicic acid/pet ether). Pet ether eluted a red band which yielded 1.25 g (3.26 mmol, 55% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-EtS})(\mu\text{-MeCO})\text{Fe}_2(\text{CO})_6$ as a red oil identified by its ^1H NMR spectrum as a 2.5/1 (e/a) mixture of two isomers.

Reaction Between Triiron Dodecacarbonyl and S-Methyl Thioacetate. (GBW-IX-35).

In 70 ml of toluene, 3.0 g (5.96 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and 0.61 g (6.76 mmol) of S-methyl thioacetate were stirred at 75°C for 21.5 h. The solvent was removed and the red oil remaining was extracted with pet ether/ CH_2Cl_2 (9/1, v/v). The extracts were filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to filtration chromatography (silicic acid/pet ether). Pet ether eluted a minor yellow band which was not collected. Further elution with pet ether/ CH_2Cl_2 (10/1, v/v) moved a red band which yielded 0.60 g (1.62 mmol, 27% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-MeS})(\mu\text{-MeCO})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid. After crystallization from pentane, mp 59-60°C, it was identified as one isomer (e, Me).

IR (CHCl_3): 2920(w), 1503(s), (acyl CO), 1426(w), 1399(w), 1340(m), 1313(w), 1109(s), 950(m), 609(s), 575(vs) cm^{-1} ;

terminal carbonyl region (pentane): 2070(s), 2028(vs),

2000(vs), 1991(vs), 1966(s) cm^{-1} .

^1H NMR (CDCl_3 , 90MHz): δ 2.25 (s, 3H, CH_3) and 2.31 (s, 3H, CH_3).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 20.9 (q, $J = 140\text{Hz}$, acyl CH_3), 46.3 (q, $J = 128\text{Hz}$, SCH_3), 209.4, 209.6, 212.0 (all s, CO) and 298.9 (s, acyl CO).

Mass spectrum, m/z (relative intensity): 370 (M^+ , 4), 342 ($\text{M}^+ - \text{CO}$, 14), 314 ($\text{M}^+ - 2\text{CO}$, 14), 286 ($\text{M}^+ - 3\text{CO}$, 16), 258 ($\text{M}^+ - 4\text{CO}$, 13), 230 ($\text{M}^+ - 5\text{CO}$, 25), 202 ($\text{M}^+ - 6\text{CO}$, 67), 187 ($\text{Fe}_2\text{S}_2\text{COCH}_3$, 6), 174 ($\text{Fe}_2\text{S}_2\text{Me}_2$, 19), 159 (Fe_2SMe , 52), 144 (Fe_2S , 100), 112 (Fe_2 , 11), 88 (FeS , 6), 56 (Fe , 36).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{Fe}_2\text{O}_7\text{S}$: C, 29.22; H, 1.64%.

Found: C, 28.95; H, 1.66%.

Reaction Between Triiron Dodecacarbonyl and S-Ethyl Thiobenzoate. (GBW-IX-37).

In 75 ml of toluene, 3.0 g (5.96 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and 1.0 g (6.0 mmol) of S-ethyl thiobenzoate were stirred at 75°C for 22.5 h. Removal of the solvent left a red oil which was taken up in pet ether/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. The solvent was again removed and the red oil applied to filtration chromatography (silicic acid/pet ether). Pet ether/ CH_2Cl_2 eluted a red band which yielded 0.68 g (1.52 mmol, 26% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-EtS})\text{-}(\mu\text{-PhCO})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid identified by its ^1H NMR spectrum as a 2.9/1 (e/a) mixture of two isomers.

Reaction Between Triiron Dodecacarbonyl and S-Ethyl Thiopivalate. (GBW-IX-32).

In 60 ml of toluene, 1.5 g (2.98 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and 0.44 g (3.0 mmol) of S-ethyl thiopivalate were stirred at 75°C for 23.5 h. Removal of the solvent left a red oil which was taken up in pet ether/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. The solvent was again removed and the red oil remaining subjected to filtration chromatography (silicic acid/pet ether). Pet ether eluted a red band which yielded 0.14 g (0.34 mmol, 11% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-Me}_3\text{CCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an air-stable red solid (one isomer, e Et) identified by comparison of its ^1H NMR spectrum to that of an authentic sample.

Reaction Between Triiron Dodecacarbonyl and an Excess of S-Ethyl Thiobenzoate. (GBW-IX-47).

In 75 ml of toluene, 3.0 g (5.96 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and 2.0 g (12.0 mmol) of S-ethyl thiobenzoate were stirred at 75°C for 24 h. Removal of the solvent left a red oil which was taken up in pet ether/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. The solvent was again removed and the red oil remaining subjected to filtration chromatography (silicic acid/pet ether). Pet ether/ CH_2Cl_2 (9/1, v/v) eluted a red band which yielded 0.64 g (1.42 mmol, 24% yield based on $\text{Fe}_3(\text{CO})_{12}$) as a red solid identified by its ^1H NMR spectrum as a 2.9/1 (e/a) mixture of two isomers.

References

1. a) Alper, H.; Chan, A.S.K. Inorg. Chem. 1974, 13, 232.
b) Alper, H.; Chan, A.S.K. J. Am. Chem. Soc. 1973, 95, 4905.
c) Dettlaf, G.; Hubener, P.; Klimes, J.; Weiss, E. J. Organomet. Chem. 1982, 229, 63.
d) Dettlaf, G.; Behrens, U.; Weiss, E. J. Organomet. Chem. 1978, 152, 95.
2. Alper, H.; Foo, C.K. Inorg. Chem. 1975, 14, 2928.
3. Benoit, A.; Le Marouille, J.Y.; Mahe, C.; Patin, H. J. Organomet. Chem. 1981, 218, C67.
4. a) Wörmsbacher, D.; Edelmann, F.; Behrens, U. Chem. Ber. 1981, 114, 153.
b) Umland, H.; Edelmann, F.; Wörmsbacher, D.; Behrens, U. Angew. Chem. Int. Ed. Engl. 1983, 22, 153; Angew. Chem. Suppl. 1983, 156.
5. a) Alper, H.; Chan, A.S.K. Inorg. Chem. 1974, 13, 225.
b) Alper, H.; Chan, A.S.K. J. Chem. Soc. Chem. Comm. 1973, 724.
6. a) Patin, H.; Mignami, G.; Benoit, A.; Le Marouille, J.Y.; Grandjean, D. Inorg. Chem. 1981, 20, 4351.
b) Patin, H.; Mignami, G.; Dabard, R.; Benoit, A. J. Organomet. Chem. 1978, 168, C21.
7. Daub, J.; Endress, G.; Erhardt, U.; Jogun, K.H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowski, J.J. Chem. Ber. 1982, 115, 1787.
8. Patin, H.; Mignani, G.; Mahe, C. J. Organomet. Chem. 1980, 197, 315.

9. a) Dean, W.K. J. Organomet. Chem. 1977, 135, 195.
b) Dean, W.K.; Vanderveer, D. G. J. Organomet. Chem. 1978, 144, 65.
10. Kruger, G.J.; Linford, L.; Raubenheimer, H.G.; Chalmers, A.A. J. Organomet. Chem. 1984, 262, 69.
11. Seyferth, D.; Henderson, R.S.; Song, L.-C. Organometallics 1982, 1, 125.
12. Seyferth, D.; Henderson, R.S. J. Organomet. Chem. 1981, 218, C34.
13. Shaver, A.; Fitzpatrick, P.J.; Steliou, K.; Butler, I.S. J. Am. Chem. Soc. 1979, 101, 1313.
14. Nametkin, N.S.; Tyurin, V.P.; Kuz'min, O.V.; Nekhaev, A.I.; Mavlonov, M.; Sideridu, A.Y. Izv. Akad. Nauk. SSSR, Ser. Khim. 1979, 2649.
15. Winter, A.; Zsolnai, L.; Huttner, G. Z. Naturforsch. 1982, 37b, 1430.
16. Müller, A.; Bhattacharyya, R.G.; Königer-Ahlborn, E.; Sharma, R.C.; Rittner, W.; Neumann, A.; Henkel, G.; Krebs, B. Inorg. Chem. Acta 1979, 37, L493.
17. a) Adams, R.D.; Golembeski, N.M. J. Am. Chem. Soc. 1979, 101, 1306.
b) Adams, R.D.; Golembeski, N.M.; Selegue, J.P. J. Am. Chem. Soc. 1981, 103, 546.
18. a) Rakowski DuBois, M. J. Am. Chem. Soc. 1983, 105, 3710.
b) McKenna, M.; Wright, L.L.; Miller, D.J.; Tanner, L.; Haltiwanger, R.C.; Rakowski DuBois, M. J. Am. Chem. Soc. 1983, 105, 5329.

19. a) Corey, E.J.; Seebach, D. Angew. Chem. 1965, 77, 1135.
b) Seebach, D. Synthesis 1969, 21.
20. Seyferth, D.; Henderson, R.S. J. Am. Chem. Soc. 1979, 101, 508.
21. Seyferth, D.; Henderson, R.S.; Song, L.-C. J. Organomet. Chem. 1980, 192, C1.
22. Seyferth, D.; Womack, G.B. J. Am. Chem. Soc. 1982, 104, 6839.
23. Adolfsson, L.; Andersson, R.; Olsson, K. Chemica Scripta 1980, 16, 122.
24. Compound 17 has been previously reported but no mp was given: Nametkin, N.S.; Tyurin, V.D.; Nekhaev, A.I.; Kondrat'eva, M.G.; Sobolev, Yu. P. Izv. Akda. Nauk SSSR, Ser. Khim. 1982, 217.
25. Gallagher, M.K. Ph.D. dissertation M.I.T., Cambridge, MA, 1984.
26. Seyferth, D.; Wood, T.G.; Fackler, J.P.; Mazany, A.M. Organometallics 1984, 3, 1121.
27. Al-Jibori, S.; Crocker, C.; McDonald, W.S.; Shaw, B.L. J. Chem. Soc., Dalton Trans. 1981, 1572.
28. Mainz, V.V.; Andersen, R.A. Organometallics 1984, 3, 675.
29. a) Dawkins, G.M.; Green, M.; Jeffery, J.C.; Stone, F.G.A. J. Chem. Soc. Chem. Comm. 1980, 1120.
b) Dawkins, G.M.; Green, M.; Jeffery, J.C.; Sambale, C.; Stone, F.G.A. J. Chem. Soc., Dalton Trans. 1983, 499.

30. Akeström, L.; Olsson, K. Chemica Scripta 1980, 16, 130.
31. Engler, V.R.; Gattow, G.; Dräger, M. Z. Anorg. Allg. Chem. 1972, 390, 64.
32. Darensbourg, D.J.; Fischer, M.B.; Schmidt, R.E., Jr.; Baldwin, B.J. J. Am. Chem. Soc. 1981, 103, 1297.
33. Engler, V.R.; Gattow, G.; Drager, M. Z. Anorg. Allg. Chem. 1972, 390, 64.
34. Binder, H.; Diamantikus, W. Z. Naturforsch. 1983, 38b, 203.
35. Schenk, W.A.; Schwietzke, T. Organometallics 1983, 2, 1905.
36. Seyferth, D.; Womack, G.B.; Song, L.-C. Organometallics 1983, 2, 928.
37. Touchard, D.; Dixneuf, P.H.; Adams, R.D.; Segmuller, B.E. Organometallics 1984, 3, 640.
38. Wei, C.H.; Dahl, L.F. Inorg. Chem. 1965, 4, 1.
39. Campana, C.F.; Yip-Kwai Lo, F.; Dahl, L.F. Inorg. Chem. 1979, 18, 3060.
40. Vahrenkamp, H.; Wolters, D. Angew. Chem. Int. Ed. Engl. 1983, 22, 154.
41. Seyferth, D.; Womack, G.B.; Cowie, M.; Hames, B.W. Organometallics 1983, 2, 1696.
42. Alper, H.; Silavwe, N.D.; Birnbaum, G.I.; Ahmed, F.R. J. Am. Chem. Soc. 1979, 101, 6582.
43. Alper, H.; Einstein, F.W.B.; Nagai, R.; Petrignani, J.F.; Willis, A.C. Organometallics 1983, 2, 1291.

44. Raubenheimer, H.G.; Kruger, G.J.; Lombard, A.
J. Organomet. Chem. 1982, 240, C11.
45. a) Coleman, J.M.; Wojcicki, A.; Pollick, P.J.; Dahl,
M.F. Inorg. Chem. 1967, 6, 1236.
b) De Beer, J.A.; Haines, R.J. J. Organomet. Chem.
1970, 24, 757.
c) Edidin, R.T.; Zyzyk, L.A.; Norton, J.R. J. Chem.
Soc. Chem. Comm. 1979, 580.
d) Patin, H.; Mignani, G.; Mahe, C.; Le Marouille, J.-Y.;
Benoit, A.; Grandjean, D. J. Organomet. Chem. 1981,
210, C1.
46. a) Yu, Y.F.; Gallucci, J.; Wojcicki, A. J. Am. Chem. Soc.
1983, 105, 4826.
b) Kampe, C.E.; Boag, N.M.; Kaesz, H.D. J. Am. Chem. Soc.
1983, 105, 2896.
c) Longato, B.; Norton, J.R.; Huffman, J.C.; Marsella,
J.A.; Caulton, K.G. J. Am. Chem. Soc. 1981, 103, 209.
d) Mott, G.N.; Granby, R.; MacLaughlin, S.A.; Taylor, N.J.;
Carty, A.J. Organometallics 1983, 2, 189.
e) Rosen, R.P.; Hoke, J.B.; Whittle, R.R.; Geoffroy, G.L.;
Hutchinson, J.P.; Zubieta, J.A. Organometallics 1984,
3, 846.
47. a) Azam, K.A.; Deeming, A.J.; Rothwell, I.P. J. Chem.
Soc., Dalton Tran. 1981, 91.
b) Blickensderfer, J.R.; Kaesz, H.D. J. Am. Chem. Soc.
1975, 97, 2681.
48. a) McKennis, J.S.; Kyba, E.P. Organometallics 1983, 2, 1249.

- b) Lindley, P.F.; Mills, O.S. J. Chem. Soc. A, 1969, 1279.
49. a) Winter, A.; Zsolnai, L.; Huttner, G. J. Organomet. Chem. 1983, 250, 409.
- b) Winter, A.; Zsolnai, L.; Huttner, G. J. Organomet. Chem. 1982, 232, 47.
50. Mayer, R.; Berthold, H. Z. Chem. 1963, 3, 310.
51. Ohno, A.; Koizumi, T.; Zsuehishashi, G. Tet. Let. 1968, 2083.
52. Bax, P.C.; Holsboer, D.H. Recl. Trav. Chim. Pays-Bas 1971, 90, 562.
53. Rylander, P.N.; Tarbell, D.S. J. Am. Chem. Soc. 1950, 72, 3021.
54. King, R.B. "Organometallic Synthesis", Academic Press: New York, 1965; Vol. 1, pp 93-95.
55. McFarlane, W.; Wilkinson, G. Inorg. Syn. 1966, 8, 181.
56. Nametkin, N.S.; Tyurin, V.D.; Kukina, M.A. J. Organomet. Chem. 1978, 149, 355.
57. Cairns, T.L.; Evans, G.L.; Larchar, A.W.; McKusick, B.C. J. Am. Chem. Soc. 1952, 74, 3982.
58. Christensen, A.T.; Witmore, W.G. Acta Cryst. B, 1969, 25, 73.
59. Christensen, A.T.; Thom, E. Acta Cryst. B, 1971, 27, 581.
60. MacGillavry, C.M.; Rieck, G.D. (ed.) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1961, Vol. III, p 276.

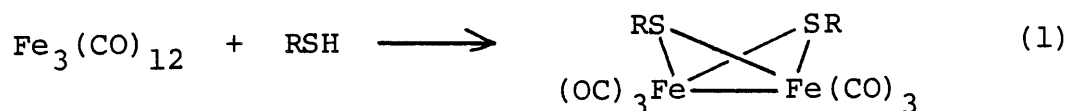
61. Rindorf, G.; Carlsen, L. Acta Cryst. B 1979, 35, 1179.
62. Henderson, R.S. Ph.D. dissertation, M.I.T., Cambridge, MA, 1981, p 105.

Chapter 4

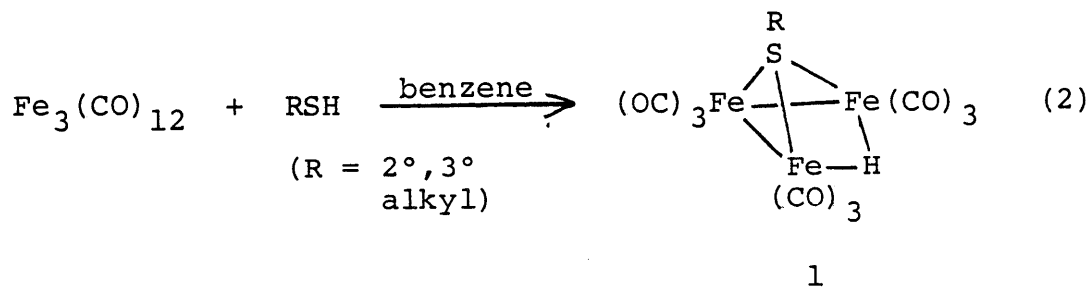
Reaction Between Triiron Dodecacarbonyl,
Alkanethiols and Triethylamine:
A New Route to Alkanethiolate
Bridged Diiron Hexacarbonyl Complexes

Introduction

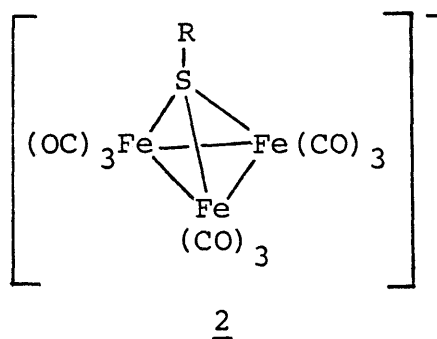
The first report concerning the reaction between organic thiols and triiron dodecacarbonyl by Hieber and Spacu¹ appeared in 1937. The products obtained from such a reaction were the dinuclear sulfido bridged complexes, $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$, (eq.1).²



Since that initial report many derivatives of this type have been prepared using this method.³ The most recent example employs α,ω -dithiols to produce complexes with alkylene units bridging the two sulfur atoms.⁴ However, in reactions with secondary and tertiary thiols a trinuclear product, 1, also could be isolated, (eq.2).^{3c,5} It was found subsequently that

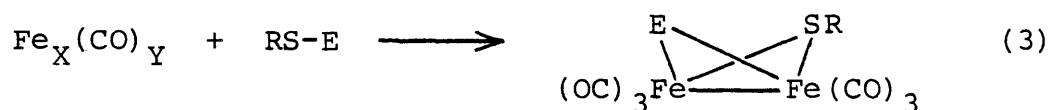


the bridging hydride of 1 (R = t-butyl, C_6H_{11}) can be removed as a proton with an amine base and the resulting anionic species, 2, reacted with a variety of electrophiles such as R_2PCl , R_2AsCl , RPCl_2 and Cl_2 to produce new $\text{Fe}_3(\text{CO})_9$ complexes.^{5,6} In related work Markó and Takács reported that sodium thiolates react with



$\text{Fe}_3(\text{CO})_{12}$ in refluxing THF to give solutions containing the sodium salt of type 2 anions.⁷

Diiron hexacarbonyl complexes containing two bridging thiolate ligands are readily accessible as presented in eq.1. However, dinuclear complexes containing a bridging RS group in conjunction with a different type of bridging ligand generally have to be isolated from the reaction of a sulfur-containing precursor in which the RS group is attached to the other bridging ligand. Reaction of such a molecule with iron carbonyls can cleave the thiolate group to produce the two bridging ligands, (eq.3). Several examples of this synthetic strategy can be

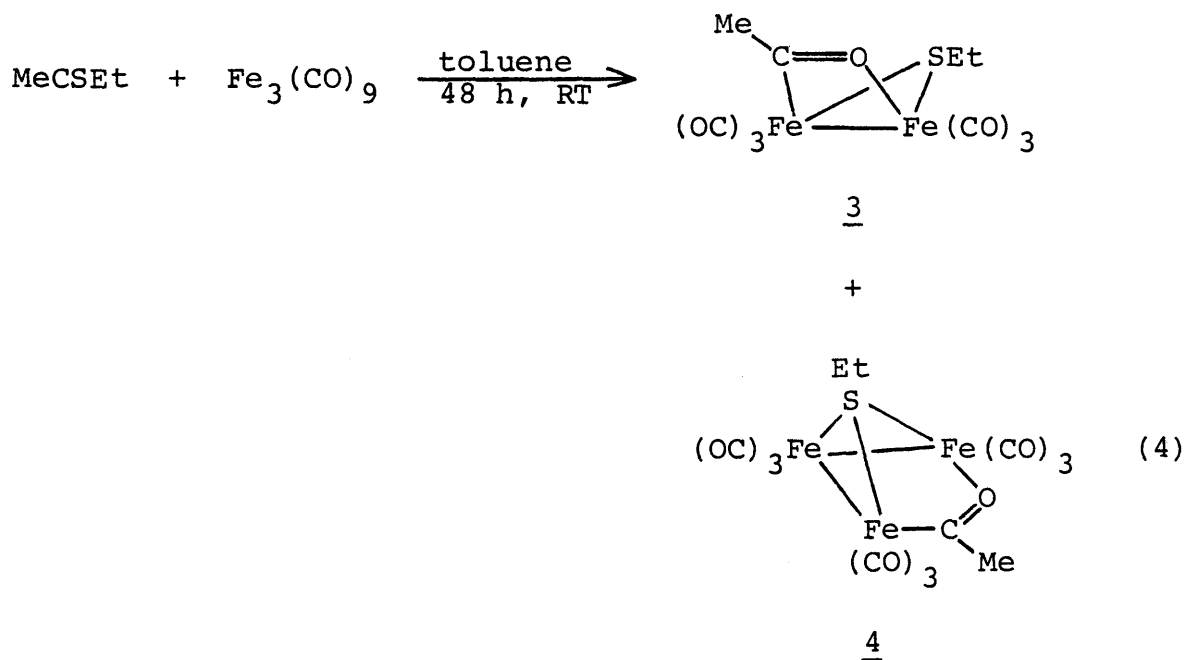


found in the literature where E is a phosphido,⁸ vinyl,⁹ $\text{R}'\text{SC}(=\text{S})-$,¹⁰ $\text{R}'\text{OC}(=\text{S})-$,¹¹ acyl,¹² or iminoacyl group.¹³ Nevertheless, these strategies generally give only moderate-to-poor yields of the desired product. This chapter will report the development of two methods for incorporating new bridging ligands into the $(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ system without the need of

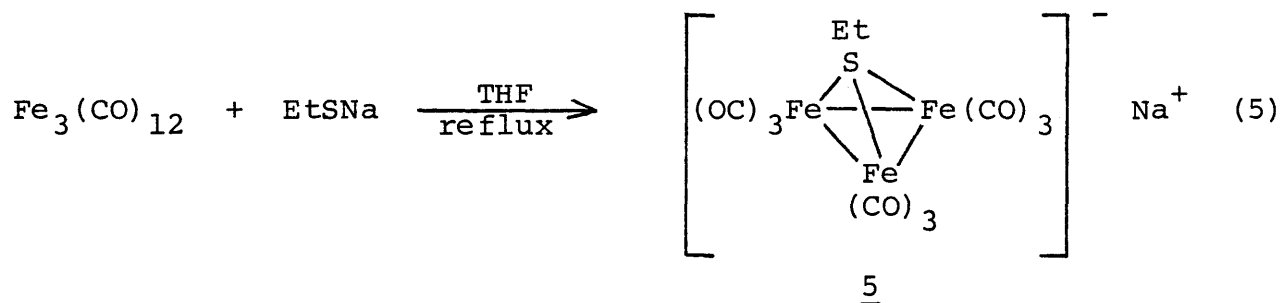
prior synthesis of RS-E type reactants.

Results and Discussion

In the previous chapter it was reported that S-alkyl monothioesters react with $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ to yield $(\mu\text{-acyl})\text{-}(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ type complexes. In only one case was a trinuclear iron complex, 4, isolated along with the bimetallic compound, (eq.4). Complex 4 was assigned the structure illustrated



with a tricapping ethanethiolate ligand since $(\mu_3\text{-RS})(\mu_2\text{-E})\text{Fe}_2(\text{CO})_9$ type complexes have been reported previously.^{6a} Compound 4, however, was the first such complex with an $\mu_2\text{-acyl}$ ligand. Due to this novel feature, it was desired to synthesize 4 by a different, independent route to confirm its assigned structure. The reaction of EtSNa and $\text{Fe}_3(\text{CO})_{12}$, which Markó had reported, generates the $[(\mu_3\text{-EtS})\text{Fe}_3(\text{CO})_9]^-$ anion, (eq.5),⁷ should allow such a synthesis. It was anticipated that the

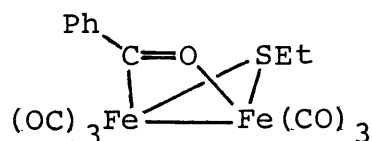


addition of acetyl chloride to a THF solution of 5 would yield 4.

For our purposes EtSNa was generated in-situ by adding ethanethiol to sodium amide in THF. Triiron dodecacarbonyl then was added to the solution and an immediate reaction ensued with brisk gas evolution and formation of a red-brown reaction mixture. This was unexpected since Markó and Takács had not reported any initial reaction at room temperature. Nevertheless, TLC analysis of the reaction mixture showed that all of the $\text{Fe}_3(\text{CO})_{12}$ had been consumed within a few minutes. Rather than refluxing the mixture, it was stirred for 1 h at room temperature and then a slight excess of acetyl chloride was added. After stirring overnight, the major product, isolated in 26% yield, was 3 (a mixture of both isomers, 2.2/1; e Et/a Et), the dinuclear acetyl complex; 4 was not formed in the reaction. Next, lithium ethanethiolate and $\text{Fe}_3(\text{CO})_{12}$ were allowed to react to see if the same results would be obtained. Since the EtSNa reaction had been vigorous at room temperature, $\text{Fe}_3(\text{CO})_{12}$ was added to an EtSLi/THF solution which had been cooled to -20°C . The resulting reaction was a little slower, but the results were the same. A red-brown solution formed and acetyl

chloride was added at -20°C . The mixture was allowed to warm to room temperature and stirred overnight. Again the red oil, 3, was isolated after filtration chromatography (silicic acid, eluting first with pentane then pentane/ CH_2Cl_2 ; 4/1, v/v) of the reaction residue in 36% yield (2.5/1; e Et/a Et).

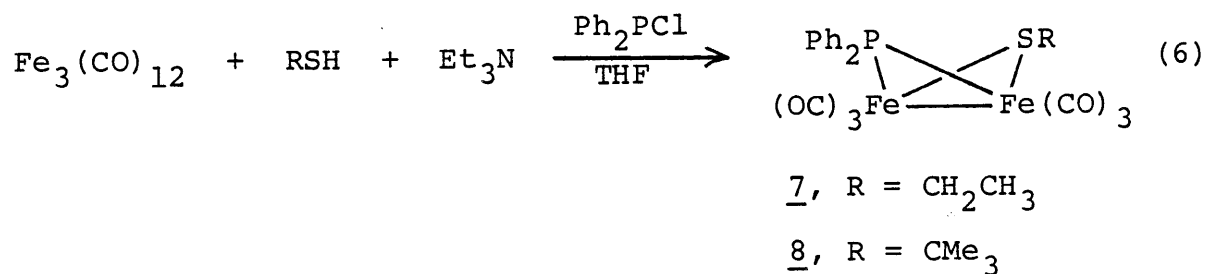
It was apparent at this time that the reaction between $\text{Fe}_3(\text{CO})_{12}$ and lithium or sodium ethanethiolate was fast and produced an anionic species which could yield diiron hexacarbonyl complexes as final products. Although these reactions had failed to yield 4, they revealed a new and potentially interesting synthetic method for generating dinuclear iron carbonyl complexes. At this point it was felt that the use of an amine to deprotonate the thiol in the presence of $\text{Fe}_3(\text{CO})_{12}$, thus avoiding the prior formation of lithium or sodium thiolates, would be overall the most convenient means of carrying out the reaction. Ethanethiol and triethylamine were added to a THF solution of $\text{Fe}_3(\text{CO})_{12}$ at room temperature. After five minutes all of the triiron dodecacarbonyl had been consumed and a red-brown solution resulted. Stirring was continued another 10 min and then an excess of acetyl chloride was added. After a reaction period of 20 h, 3 was isolated in 52% yield as a 3/1 (e Et/a Et) mixture of geometric isomers. Following the same procedure, benzoyl chloride was used as the quenching electrophile and an 83% yield of 6 was isolated as a 2.3/1 (e Et/a Et) mixture of both isomers. Both 3 and 6 have been synthesized previously by the reaction of the corresponding S-alkyl thioester and $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$.¹² This new method of generating



6

3 improved the yield a little over the 51% obtained from the direct $\text{Fe}_3(\text{CO})_{12}/\text{MeC(O)SEt}$ reaction. However, that of 6 was dramatically increased from 27% to 83% by use of the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ system. This new synthesis of 3 and 6, however, not only provided reasonable yields of the μ -acyl complexes but also was more convenient in that the synthesis and isolation of the S-alkyl thioesters was eliminated.

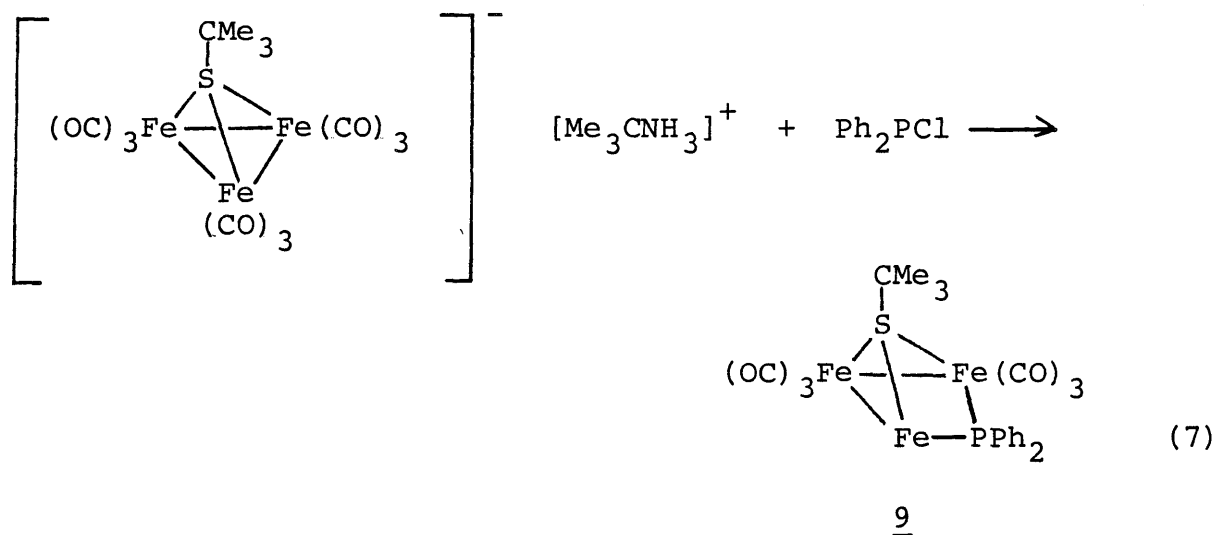
Realizing that acetyl and benzoyl chloride are electrophilic reagents which in the products 3 and 6 had provided bridging 3-electron donating ligands, we turned our attention to introducing electrophiles into the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ reaction mixture which could potentially provide the same type of ligands. Thus diphenylchlorophosphine was added to such a reaction mixture. After stirring 20 h, the red-brown solution had become dark red and a white precipitate ($[\text{Et}_3\text{NH}]\text{Cl}$) had formed. From this solution the diiron hexacarbonyl complex, 7, was isolated in 80% yield, (eq.6). This compound was an



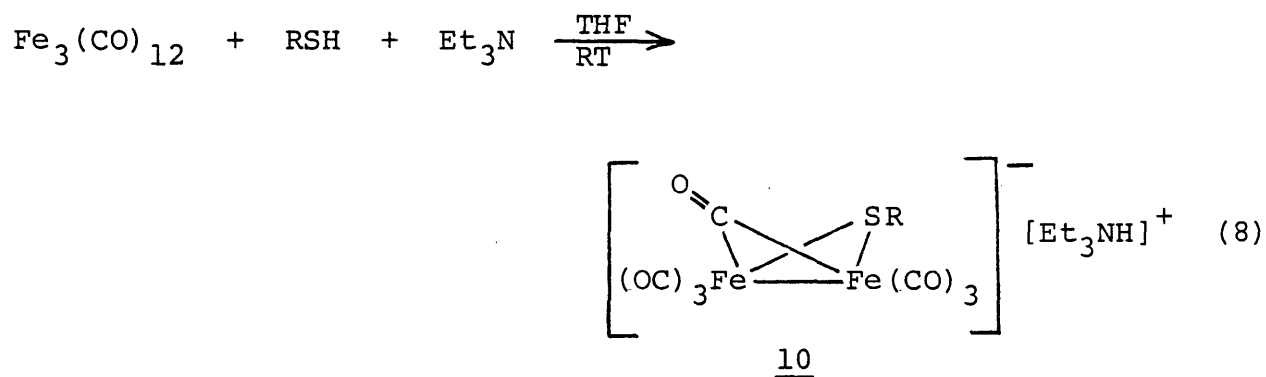
orange, air-stable solid, mp 111-112°C, which by its ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum proved to exist as only one isomer (e Et); δ_{P} 142.9. In like manner, $(\mu\text{-Me}_3\text{CS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$, 8 was isolated from the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reaction mixture in 91% yield. It too was an orange solid, mp 137-139°C, and existed as one isomer (e CMe_3), δ_{P} 139.8. The orientation of the alkyl group attached to sulfur as being in the equatorial position is favored since it avoids the sterically demanding situation of having it in the axial position. In the related $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ complexes the di-axial isomer (a,a) has never been observed, except when $\text{R}=\text{H}$,¹⁴ due to steric constraints.¹⁵

The reaction of t-butanethiol with $\text{Fe}_3(\text{CO})_{12}$ in the presence of triethylamine proceeded analogously to the observations made with the ethanethiol system to produce a red-brown mixture which, as indicated by the isolation of 8, contained the same type anionic intermediate. Previously, $(\mu\text{-RS})(\mu\text{-R}'_2\text{P})\text{-Fe}_2(\text{CO})_6$ type compounds have been synthesized by treating the appropriate thiophosphorus precursor, $\text{R}_2\text{P-SR}'$ with one of the iron carbonyl species.⁸ The synthesis of 7 and 8 accomplishes the same result without the need of a preformed thiophosphorus compound.

It appeared from these reactions that a triiron nonacarbonyl complex like 2 or 5 was not the anionic species being formed in the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system. Huttner and co-workers have shown that 2, an anionic triiron thiolate complex, reacts with diphenylchlorophosphine with retention of the trinuclear framework to yield 9, (eq.7). Since only the bimetallic

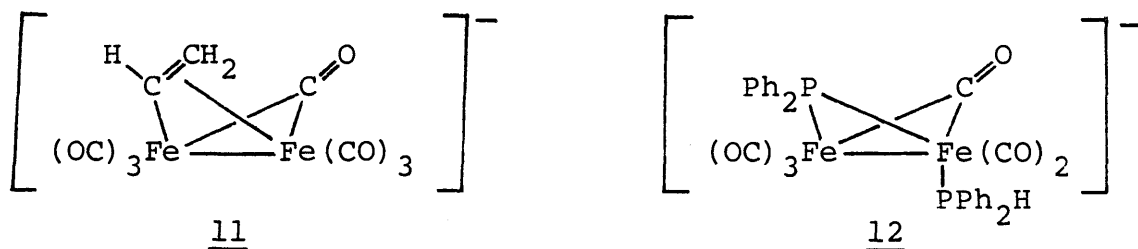


complexes 7 and 8 were isolated from the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ ($\text{R} = \text{Et}, \text{CMe}_3$) reaction mixtures when quenched with Ph_2PCl , it is apparent that a trinuclear iron complex is not the nucleophile involved in these reactions. Rather, a dinuclear anionic species, 10, seems much more reasonable as the active agent formed in these systems, (eq.8). Related complexes 11



and 12 have been reported recently, providing literature precedent for the proposed formation of 10. Further proof for the intermediacy of 10 is provided by IR spectra of the THF reagent solutions generated from the reaction of EtSLi , EtSNa

and EtSH/Et₃N with triiron dodecacarbonyl. Table 1 reports the bands found in the bridging $\nu(\text{CO})$ region of these IR spectra and compares them with those reported for the related complexes 11^{16a} and 12.^{16b} The IR spectra of the Na⁺ and Li⁺



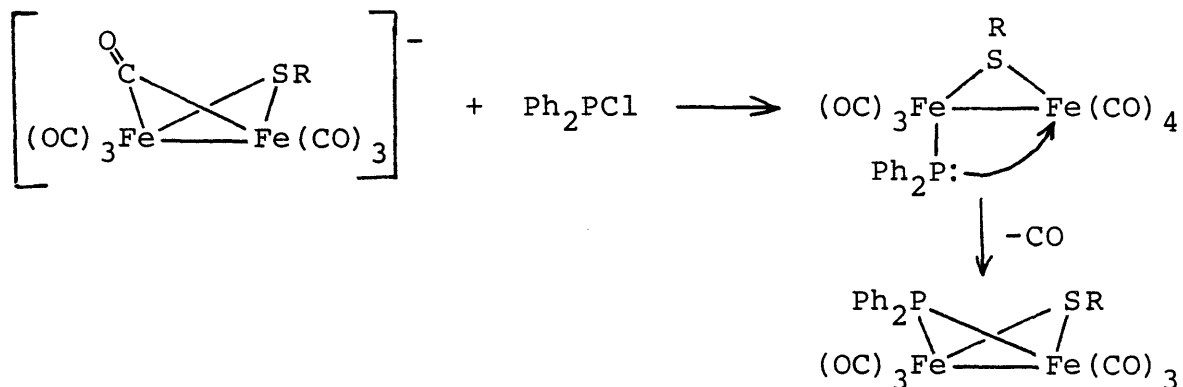
salts of 10 revealed two bands assigned to bridging carbonyl vibrations. In the [10]⁻[Et₃NH]⁺ complex only the higher wave-number band was observed at 1743 cm⁻¹. The lower frequency bands of [10]⁻Na⁺ and [10]⁻Li⁺ are no doubt due to ion pairing of the metal cation at the μ -CO oxygen atom. The higher wave-number absorption bands, which are independent of the cation, are attributed to the free anion.¹⁷

The formation of compounds 3, 6, 7 and 8 now can be rationalized as proceeding by nucleophilic attack at the electrophile, followed by bridging of the new ligand with elimination of carbon monoxide, Scheme 1. When Ph₂PCL, which reacts faster than the acid chlorides, was used as the electrophile, gas evolution from the reaction mixture was observed. The potential of the Fe₃(CO)₁₂/RSH/Et₃N system to produce diiron hexacarbonyl complexes with a bridging thiolate ligand thus was established and needed only to be exploited.

Electrophiles which could form bridging, 3-electron donor

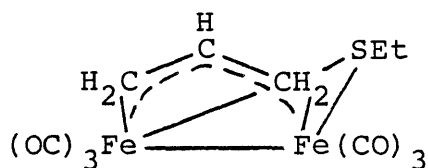
Table 1. IR Data for the $[(\mu-E)(\mu-CO)Fe_2(CO)_6]^-$ Anions.

<u>Compound</u>	<u>Cation</u>	<u>$\nu(\mu-CO)$</u>	<u>Solvent</u>
<u>10</u>	Et ₃ HN	1743	THF
<u>10</u>	Na	1745 1697	THF
<u>10</u>	Li	1745 1670	THF
<u>11</u>	Ph ₄ P	1735	CH ₂ Cl ₂
<u>12</u>	Li	1645	THF
<u>12</u>	PPN	1710	THF



Scheme 1

ligands continued to be the focus of this work. Thus allyl chloride was added to the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ mixture. The same experimental observations were noted as described before; the solution became red and a white precipitate formed. A red, crystalline solid, mp 41-42°C, was obtained in 80% yield after filtration chromatography (silicic acid/pentane) of the reaction mixture. Based on the isolation of the μ -acyl and μ -phosphido complexes, this new product was assumed to be a diiron complex with a bridging allyl ligand, 13. The mass



13

spectrum of this solid, which showed peaks for the parent ion and successive loss of six carbonyl ligands, and the combustion analysis confirmed at least that it had the elemental

composition of 13. The ^{13}C NMR spectrum indicated that the allyl ligand was bound symmetrically in the complex; a signal for the two allyl methylene carbon atoms appeared as a triplet at δ_{C} 20.9 ($J = 154\text{Hz}$). In the ^1H NMR spectrum, the allyl protons were observed as a multiplet at δ 4.76 and two doublets at δ 0.47, $J(\text{HH anti}) = 12.6\text{Hz}$, and δ 1.97, $J(\text{HH syn}) = 7.5\text{Hz}$, corresponding to the anti and syn hydrogens. The coupling constants for the anti and syn allyl protons compare well with those reported for two dinuclear palladium complexes containing bridging allyl ligands.^{18,19} Transition metal compounds with μ -allyl functions are not plentiful,²⁰ but X-ray diffraction studies have been accomplished for several compounds with this ligand bridging both bonded^{18,19,21} and non-bonded metal centers.²²

Desiring to confirm unambiguously the presence of a μ -allyl ligand, an X-ray diffraction study of 13 was undertaken. Single crystals of 13 suitable for this purpose were grown from a methanol solution at -20°C . The structure determination of 13 confirmed it was a diiron hexacarbonyl complex with both an ethanethiolate ligand and allyl ligand bridging between the two metals, Figure 1. The thiolate ligand is bound slightly asymmetrically across the metals [$\text{Fe}(2)\text{-S} = 2.251(\text{a})\text{\AA}$; $\text{Fe}(1)\text{-S} = 2.235(2)\text{\AA}$] as is the allyl ligand [$\text{Fe}(1)\text{-C}(3) = 2.119(2)\text{\AA}$; $\text{Fe}(2)\text{-C}(5) = 2.139(5)\text{\AA}$], although this deviation from symmetry was not great enough to be detected spectroscopically. The plane of the allyl carbon atoms is tilted by 6.53° with respect to the Fe-S-Fe plane with C(4) being tipped slightly toward

Figure 1. ORTEP diagram of 13 showing the 40% probability thermal ellipsoids and the atom labelling scheme. Hydrogen atoms are drawn as arbitrary spheres with $\beta = 1.0 \text{ \AA}^2$.

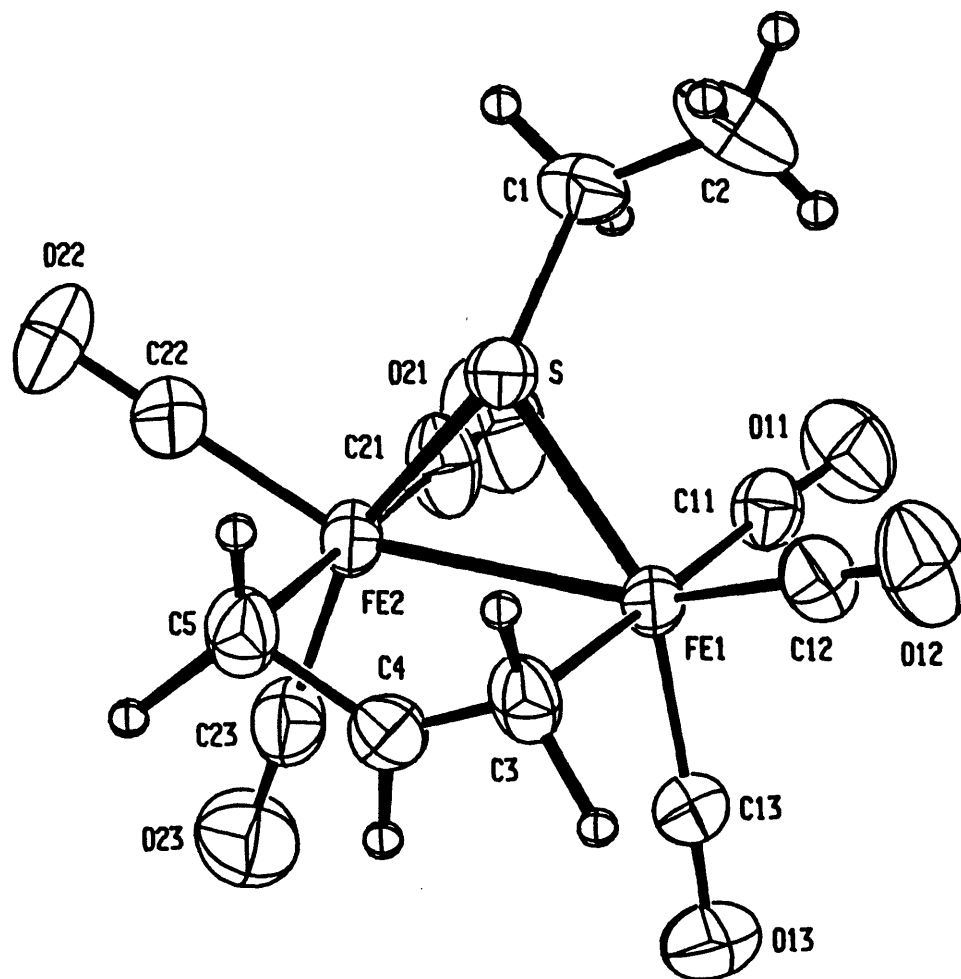
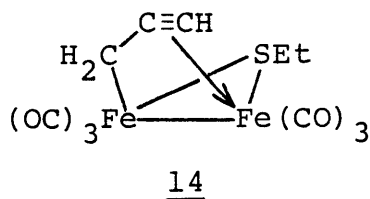


Table 2. Same Interatomic Distances and Angles (deg) for 13.

<u>(i) Interatomic Distances (Å)</u>	<u>(ii) Bond Angles</u>
Fe(1)-Fe(2) = 2.675(1)	Fe(1)-S-Fe(2) = 73.2(1)
Fe(1)-S = 2.235(2)	Fe(1)-C(3)-C(4) = 89.6(3)
Fe(1)-C(3) = 2.119(5)	Fe(1)-Fe(2)-S = 53.1(1)
Fe(1).....C(4) = 2.546(4)	Fe(1)-Fe(2)-C(5) = 89.9(1)
Fe(2)-S = 2.251(2)	Fe(1)-S-C(1) = 86.2(1)
Fe(2)-C(5) = 2.139(5)	Fe(2)-Fe(1)-S = 53.7(1)
Fe(2).....C(4) = 2.445(4)	Fe(2)-Fe(1)-C(3) = 86.2(1)
S-C(1) = 1.823(5)	Fe(2)-S-C(1) = 113.6(2)
C(1)-C(2) = 1.513(9)	C(3)-C(4)-C(5) = 126.3(7)
C(3)-C(4) = 1.426(8)	C(4)-C(5)-Fe(2) = 84.3(3)
C(4)-C(5) = 1.414(8)	
Fe-CO(mean) = 1.784	
C-O(mean) = 1.137	

the latter plane. The carbon-carbon distances of the allyl unit $[C(3)-C(4) = 1.426(8)\text{\AA}; C(4)-C(5) = 1.414(3)\text{\AA}]$ lie between the values reported for single and double carbon-carbon bonds indicating the ligand is best regarded as a delocalized π -allyl ligand.

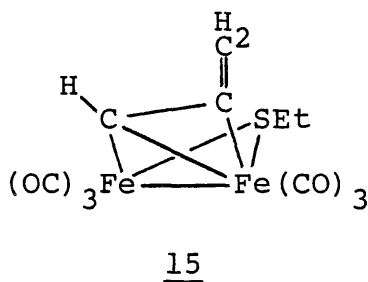
Having successfully carried out this reaction of allyl chloride with the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system, other organic electrophiles with π -systems which could allow the formation of similarly bridging ligands were investigated. Propargyl bromide, which has an obvious similarity to allyl chloride, was allowed to react with the $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^- [\text{Et}_3\text{NH}]^+$ species. The solution was stirred for 20 h after which time a red, crystalline solid, mp $39\text{-}41^\circ\text{C}$, was isolated in 91% yield. Extrapolating from compound 13, this new product was expected to contain a three-carbon bridging propargyl ligand as depicted by 14. Simple σ, π -acetylide ligands are known to bridge the



two metals of $(\mu\text{-R}_2\text{P})(\mu\text{-R}'\text{C}\equiv\text{C})\text{Fe}_2(\text{CO})_6$ complexes,²⁴ making 14 a reasonable expectation. Curiously, the ^1H NMR spectrum (CD_2Cl_2 , 90MHz) revealed the methylene protons to be equivalent, occurring as a doublet ($J = 4.9\text{Hz}$), due to long range coupling, at δ 5.30. The methine proton produced a triplet ($J = 4.9\text{Hz}$) at δ 7.39. If the propargyl ligand was bound as shown in 14,

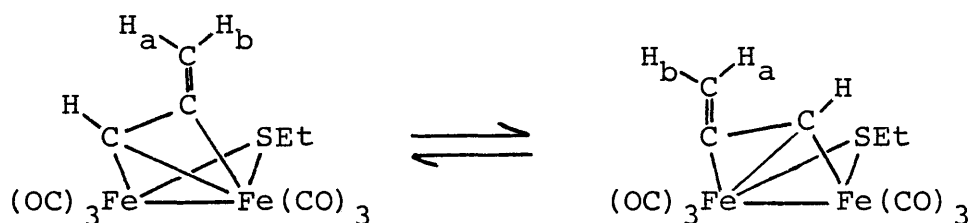
the methylene protons would definitely be magnetically inequivalent, unless a fluxional process which could equilibrate them was in operation. The ^{13}C NMR spectrum did not provide conclusive information for or against 14; the propargyl carbon signals appeared at δ_{C} 93.4 (t, $J = 167\text{Hz}$), 114.8 (d, $J = 162\text{Hz}$) and 176.6(s) with the expected proton-coupling patterns.

A structural alternative to 14, for which a reasonable fluxional process to equilibrate the propargyl CH_2 protons could be postulated, is depicted by 15. Complex 15 represents



a situation in which the organic ligand is best described as a μ -allenyl unit. The methylene group is not bound to the metals at all, instead the ligand is bound like a bridging σ, π -vinyl group.²⁵ A fluxional process of μ -vinyl ligands by which they change π -coordination from one metal to the other has been suggested to explain the dynamic behavior of these ligands.²⁶ Such a process for 15 would equilibrate the two methylene hydrogens as they exchange positions when the ligand flips from one metal to the other, Scheme 2.

Since the mass spectrum and combustion analysis confirmed that the product had the correct elemental composition, an



Scheme 2

X-ray diffraction study was desired to resolve the structural question. Crystals suitable for this purpose, however, could not be obtained. The problem was easily resolved by adding propargyl bromide to the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ system from which a red, crystalline solid, 16, was isolated in 92% yield mp 56-58°C. The ^1H and ^{13}C NMR spectra (Table 3) confirmed that the propargyl ligand in this material was bound in the same manner as in the first derivative. Again the propargyl CH_2 protons were equivalent in the ^1H NMR spectrum, appearing as a triplet ($J = 4.4\text{Hz}$) at δ 5.39.

The X-ray diffraction study of 16 proved that the propargyl group was bound as depicted by 15, Figure 2. As in 13 the thiolate ligand bridges the two iron atoms slightly asymmetrically with Fe-S distances of 2.283(2) and 2.250(2) Å. Complex 16 has the same basic structural features reported for other η^1, η^2 -vinyl bridged $\text{Fe}_2(\text{CO})_6$ systems.²⁷ The Fe-Fe distance of 2.550(1) Å is significantly shorter than the 2.675(1) Å distance in 13; this probably reflects the difference in bite sizes of the two organic bridges (i.e., diatomic as opposed to triatomic). The C(6)-C(7) distance of 1.335(9) Å is a

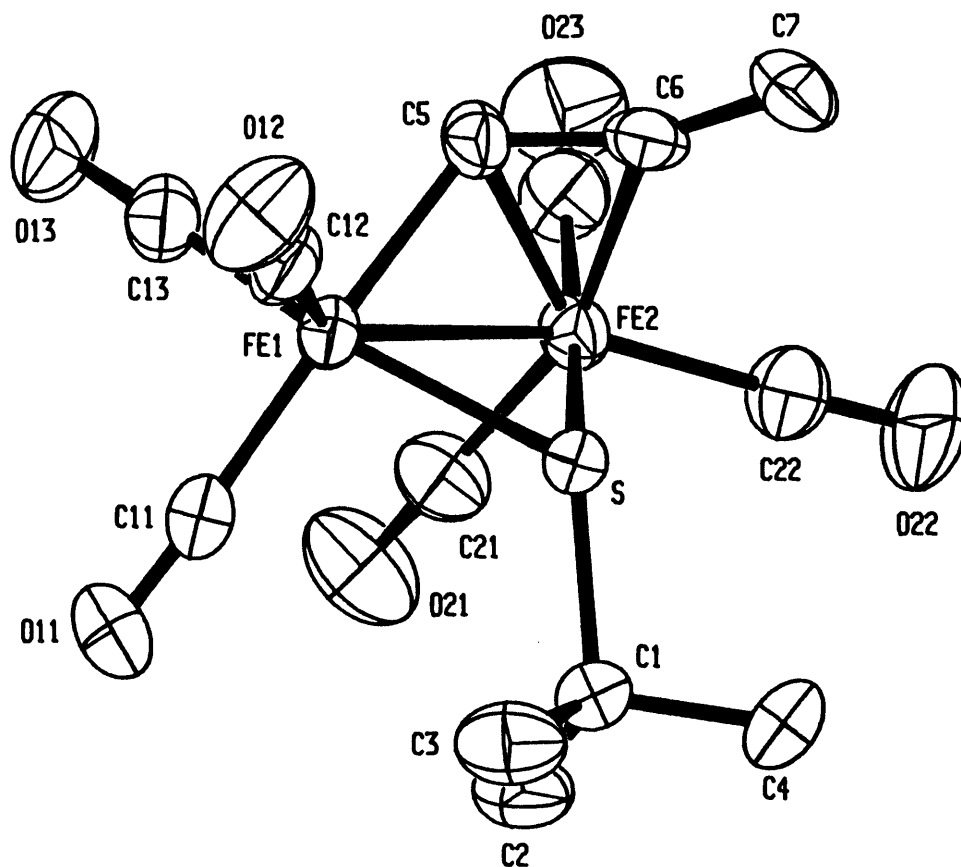


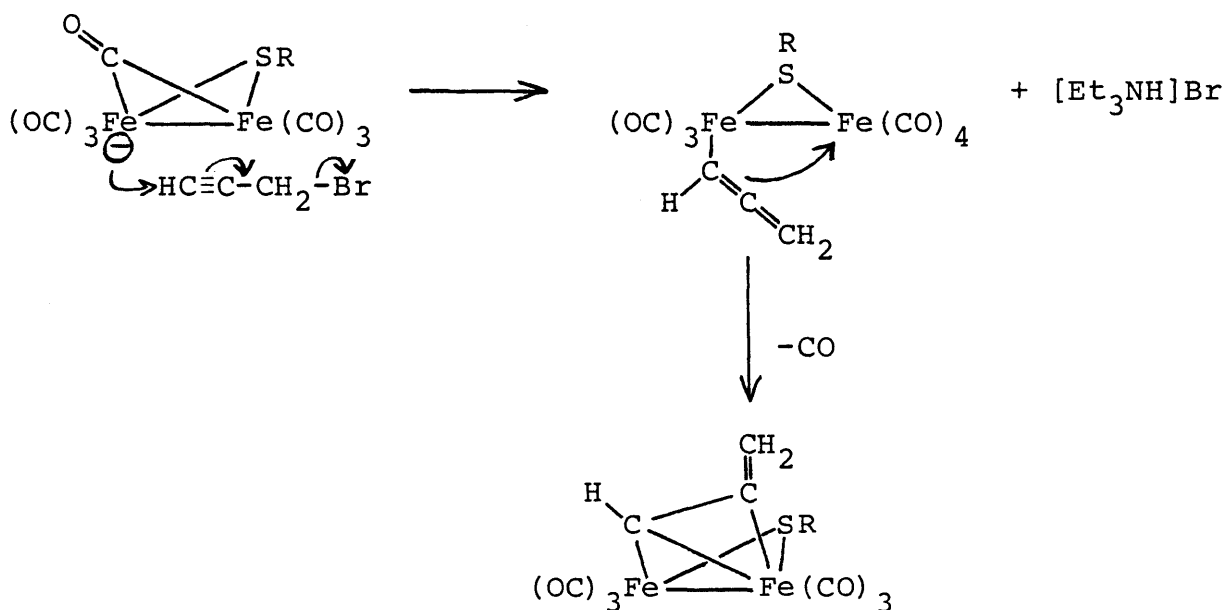
Figure 2. ORTEP diagram of 16 showing the 40% probability thermal ellipsoids and the atom labelling scheme.

Table 3. Relevant Bond Lengths (\AA) and Angles for 16.

<u>(i) Bond Lengths</u>	<u>(ii) Bond Lengths (deg)</u>
Fe(1)-Fe(2) = 2.550(1)	Fe(1)-C(5)-Fe(2) = 77.5(2)
Fe(1)-S = 2.250(2)	Fe(1)-C(5)-C(6) = 124.1(5)
Fe(1)-C(5) = 1.982(6)	Fe(1)-Fe(2)-C(5) = 49.4(2)
Fe(2)-S = 2.283(2)	Fe(1)-Fe(2)-C(6) = 78.3(2)
Fe(2)-C(5) = 2.091(6)	Fe(1)-Fe(2)-S = 55.2(1)
Fe(2)-C(6) = 2.125(6)	Fe(1)-S-C(1) = 121.9(2)
S-C(1) = 1.867(6)	Fe(2)-Fe(1)-S = 56.4(1)
C(1)-CH ₃ (mean) = 1.522	Fe(2)-C(5)-C(6) = 72.5(4)
C(5)-C(6) = 1.363(9)	Fe(2)-C(6)-C(5) = 69.8(4)
C(6)-C(7) = 1.335(9)	Fe(2)-S-C(1) = 119.5(2)
Fe-CO(mean) = 1.780	C(5)-Fe(1)-S = 83.0(2)
C-O(mean) = 1.144	C(5)-C(6)-C(7) = 156.7(7)
	C(5)-Fe(2)-C(6) = 37.7(2)

standard carbon-carbon double bond length,²³ while the C(5)-C(6) distance of 1.363(9) Å is elongated due to π -coordination to Fe(2). This distance is comparable to the C-C bond distance of other μ -vinyl groups.^{25a,b,26b,27}

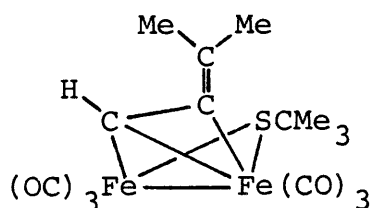
Since the methylene groups of the propargyl bromide quench was not bound to the metals in 15 and 16, the first contact between the active metal species and quench probably occurs at the alkyne function as in an S_N2' mechanism, Scheme 3. If direct halide substitution had occurred (S_N2), it would



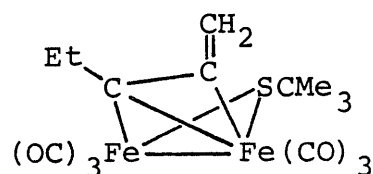
Scheme 3

require the eventual cleavage of the Fe-CH₂ bond formed or transfer of a hydrogen from this unit to the other terminal carbon to allow isolation of the μ -allenyl species. Addition of 3-bromo-3-methyl-1-butyne ($HC\equiv CMe_2Br$) to the $Fe_3(CO)_{12}$

Me₃CSH/Et₃N system resulted in the isolation of 17 after 4.5 h as a red solid in 95% yield. The ease with which 17 was formed is in harmony with an S_N2' type mechanism, although an S_N1 process is not excluded. The presence of an ethyl group on the alkynyl carbon as in 1-chloro-2-pentyne (EtC≡CCH₂Cl) did not adversely affect the course of the reaction either. Complex 18 was isolated in 77% yield after a reaction period of 4 h.



17

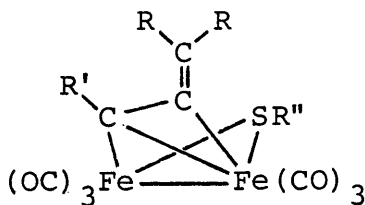


18

These compounds were confirmed to have the μ-allenyl structure by the chemical shifts of their allenyl ligand carbons in the ¹³C NMR spectra (Table 4) which harmonize with the values found for 15 and 16.

The ¹H NMR spectra of 17 and 18 showed that they too had fluxional allenyl ligands. For 17 the two allenyl methyl groups were equivalent at room temperature, giving rise to a singlet at δ 1.81 (toluene-d₈). The spectrum of 18 revealed two broad peaks at δ 2.55 and 5.20, both integrating for two protons, corresponding to the ethyl and allenyl CH₂ groups, respectively. This indicates that the fluxional process for 18 is slower than that for 15, 16 and 17 for which the fast exchange ¹H NMR spectra were obtained at room temperature. A variable temperature

Table 4. ^{13}C NMR Data for the μ -Allenyl Complexes.^{a, b}



R'^b	R	R''	$\delta_{\text{C}}(\text{Fe}_2\text{CR})$	$\delta_{\text{C}}(\text{Fe}-\text{C}=\text{C})$	$\delta_{\text{C}}(=\text{CR}_2)$
H	H	Et	114.8 (d, $J = 162\text{Hz}$)	176.6	93.4 (t, $J = 167\text{Hz}$)
H	H	CMe_3	113.2 (d, $J = 162\text{Hz}$)	177.7	95.5 (t, $J = 166\text{Hz}$)
H^c	Me	CMe_3	148.6	177.1	94.7 (t, $J = 163\text{Hz}$)
Et	H	CMe_3	119.6 (d, $J = 161\text{Hz}$)	171.8	115.4

^aPeaks reported in ppm downfield from internal tetramethylsilane.

^bSolvent used was C_6D_6 .

^cSolvent used was CD_2Cl_2 .

^1H NMR study of 17 confirmed the dynamic behavior of this compound. As the temperature was lowered the singlet of the allenyl CH_3 groups broadened until two peaks became observable below -23°C , Figure 3. The limiting low temperature spectrum was obtained at -53°C where the methyl groups give rise to two sharp singlets at δ 1.88 and 1.75. The t-butyl group remains a sharp singlet over the entire temperature range at δ 1.07. From these spectra an approximate energy of activation for this fluxional process could be calculated as $\Delta G^\ddagger = 12.4 \text{ kcal mol}^{-1}$, assuming a coalescence temperature of -23°C .²⁸ This ^1H NMR study indicates that the dynamic process depicted in Scheme 2 is operating in these complexes. It has been suggested recently that μ_2 -acetylide²⁹ and μ_2 -acyl³⁰ ligands can also display this same type fluxional behavior.

The μ -allyl and μ -allenyl complexes thus far reported potentially can exist as two isomers with the thiolate alkyl group oriented in either the axial or equatorial position. However, only one isomer was ever found to exist for any of these compounds, unlike the μ -acyl complexes 3 and 6, for which both possible isomers were observed by NMR spectroscopy. The ^{13}C NMR data for 3 and 6 also revealed that the SCH_2 carbon signals appear at $\sim\delta_{\text{C}}$ 33.0 for the equatorial ethyl group and at $\sim\delta_{\text{C}}$ 26.0 for the axial. For the compounds other than 3 and 6 with μ -SEt ligands, the ^{13}C NMR spectra confirm that the ethyl groups occupy the equatorial position as evidenced by a signal for each around δ_{C} 33.0 which can be assigned to the SCH_2 carbon. For the compounds which contain a μ - Me_3CS ligand,

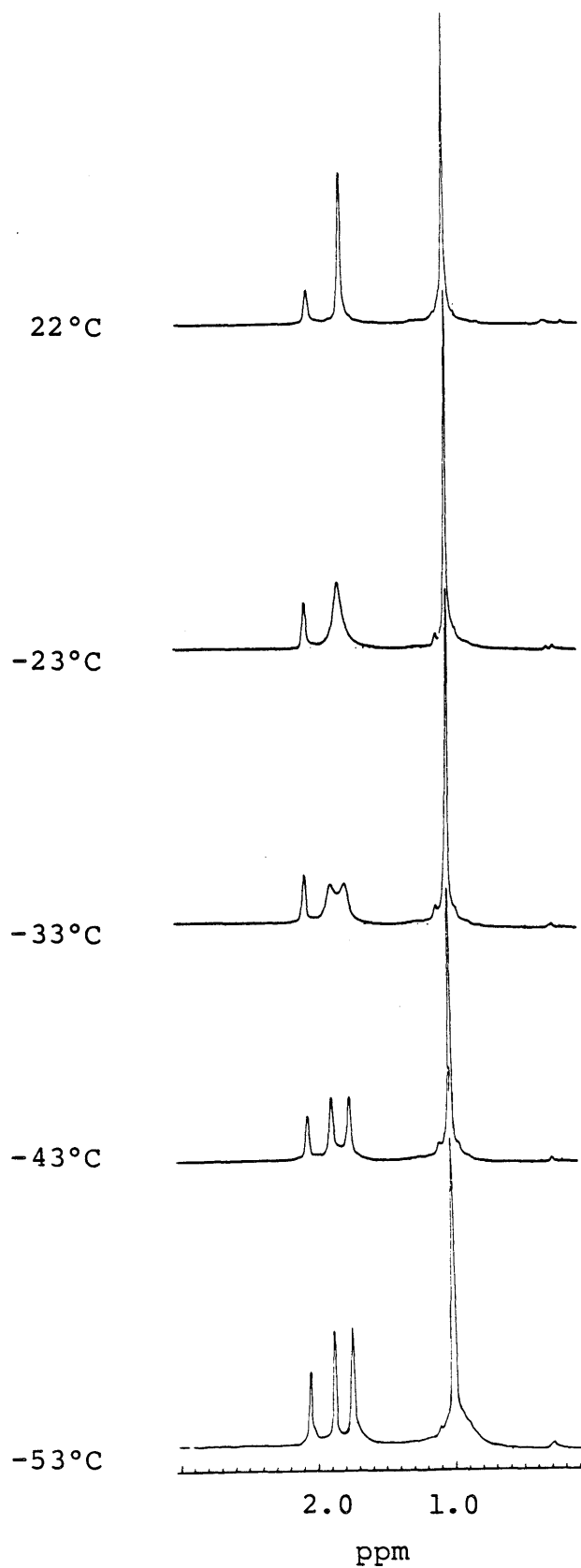


Figure 3. Variable temperature ^1H NMR spectra of $(\mu\text{-Me}_2\text{C}=\text{C}=\text{CH})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$, 17, (toluene- d_8).

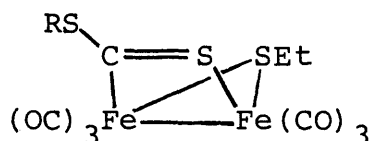
the orientation of the t-butyl group also is considered to be equatorial as in the case of the μ -SEt complexes.

Interested still in the reaction of organic electrophiles with the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system, bromoacetone was added to this reagent solution ($\text{R} = \text{Et}$). The reaction mixture was stirred overnight; however, the solution remained brown-red and no ammonium salt precipitated. These observations indicated that no reaction had occurred. Removal of the solvent and chromatographic work-up (silicic acid/pentane) of the reaction residue gave only an 18% yield of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ as a 2/1 (e,a/e,e) mixture of isomers. This was surprising in view of the ready formation of the μ -allyl and μ -allenyl complexes. The reaction was thus repeated at reflux. The mixture was refluxed for 1 h but only $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ was again isolated in 43% yield (based on $\text{Fe}_3(\text{CO})_{12}$).

Another reactive alkyl halide, benzyl chloride, which has the potential of forming a 3-electron donor, bridging ligand, was next tried. It was added to the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reaction mixture and after stirring for 4 h TLC analysis of the solution showed no product formation. At this point, carbon disulfide was added to the mixture which resulted in an immediate reaction. The solution became dark red and the ammonium salt precipitated. From this reaction mixture, 19 was isolated in 94% yield. The synthesis of 19 was not unexpected. A few structurally analogous compounds have been reported, isolated from the reaction of $\text{Fe}_2(\text{CO})_9$ and trithiocarbonates. An X-ray diffraction study of one such product has been reported.¹⁰

However, the formation of 19 does indicate that an interaction between the benzyl chloride and active metal species had not occurred since the benzyl group in 19 was attached to the exo sulfur atom of the incorporated carbon disulfide.

In general, addition of CS₂ to the Fe₃(CO)₁₂/EtSH/Et₃N system prior to addition of the alkyl halide gave the same final result. The solution became red and the IR spectrum of the mixture showed ν(CO) bands in the terminal carbonyl ligand region, 2060 to 1980 cm⁻¹, but no bands in the ν(μ-CO) region indicating the disappearance of the original anionic metal complex. After 1 h iodomethane was added forming 20 which was

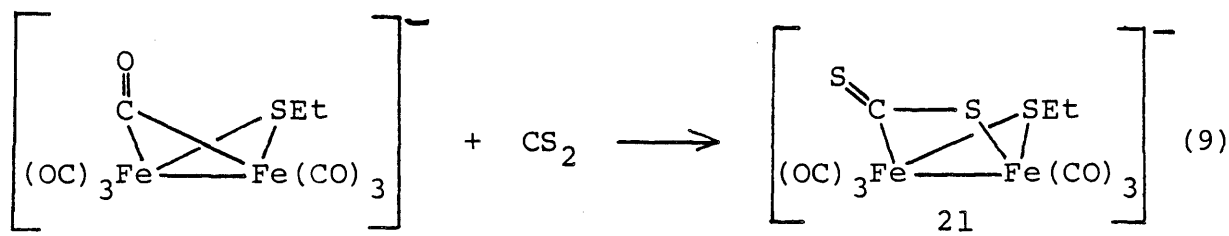


19, R = CH₂Ph

20, R = Me

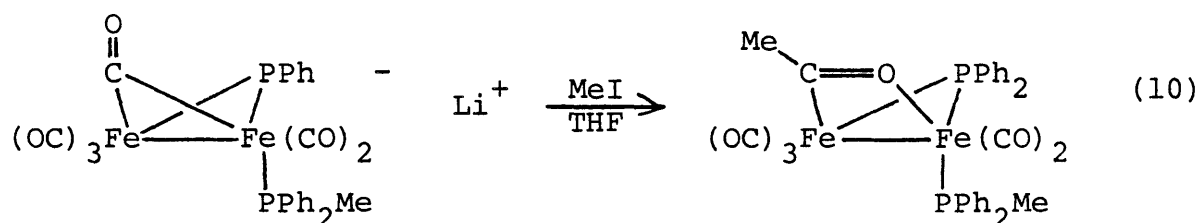
isolated in 96% yield after 2.5 h.

The IR spectra of the reaction mixture prior to the addition of MeI indicated that a CS₂ adduct had been formed and that the bridging carbonyl function had been lost. We postulate that the reactive intermediate is 21, a μ-CS₂ complex, from which 19 and 20 could be easily formed, (eq.9). The spectral



data for 19 and 20 confirm their structures. Their mass spectra and combustion analyses agree with this composition and the low field carbon resonances of the thiocarbonyl carbon in the ^{13}C NMR spectra (δ_{C} 304.6 for 19 and δ_{C} 306.0 for 20) are in harmony with the shifts reported for analogous complexes.¹⁰

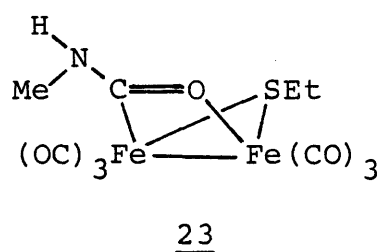
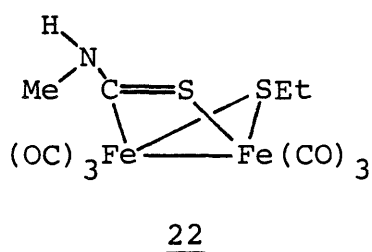
A simple alkyl halide, iodomethane, also failed to react with the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ system, both at room temperature and reflux. This was unexpected since Wojcicki and coworkers have reported that related diiron anionic species will react with alkyl halides to yield bridging acyl ligands, (eq.10).^{16b,31}



It would appear that the phosphido bridged complexes being investigated by these workers are stronger nucleophiles than the thiolate bridged species under consideration here.

Nevertheless, the successful reaction of carbon disulfide with the $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ anion suggested other heterocumulenes as potential reactants. Thus methyl isothiocyanate was added to the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ system and after stirring for 30 min, addition of iodomethane followed. The reaction solution was stirred for 20 h after which time a red, crystalline solid, mp 127-128°C dec, was isolated in 89% yield. This material, however, did not contain the expected dimethyl thio-carbamoyl ligand. Despite the presence of iodomethane in the

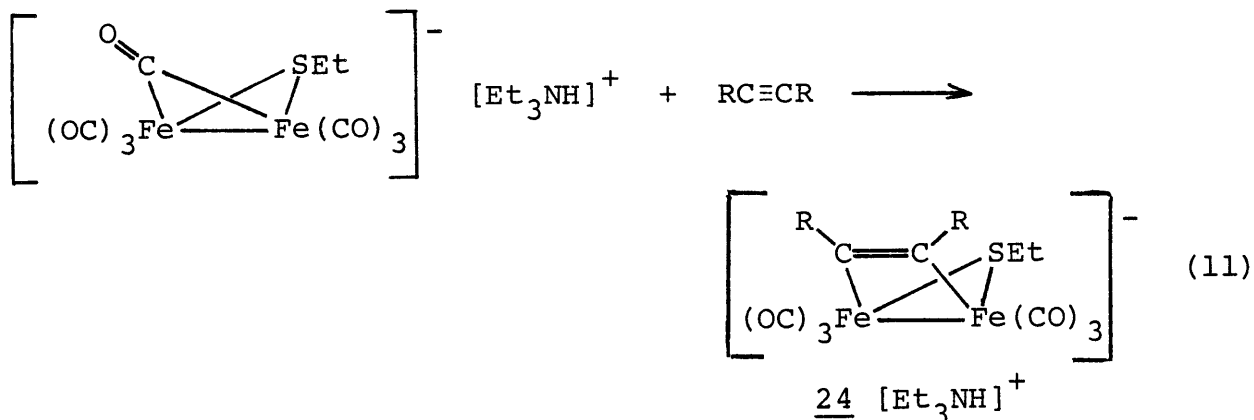
reaction mixture, a mono-methyl thiocarbamoyl complex 22 had formed. The ^1H NMR spectrum of 22 showed the N-CH_3 proton signal as a doublet ($J = 4.9\text{Hz}$) at δ 3.0 and the amine hydrogen resonance as a broad peak at δ 7.29. The same result was obtained with methyl isocyanate, although this compound failed to react at room temperature over a 27 h period (indicated by the fact that when CS_2/MeI was added at this point the formation of 20 in 61% yield was observed). In a second reaction CH_3HCO gave 23 in 33% yield after the reaction mixture had been refluxed for 30 min. The ^1H NMR spectrum of compound 23 also



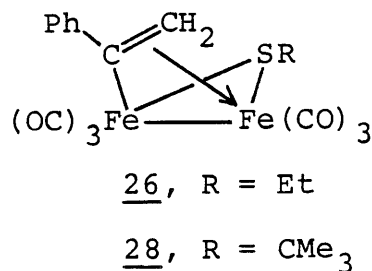
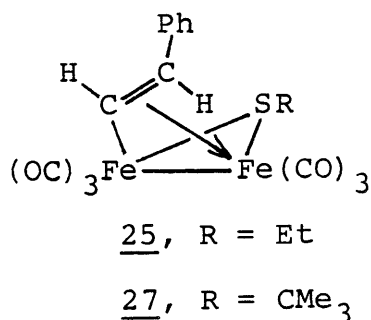
displayed a doublet ($J = 4.9\text{Hz}$) at δ 2.55 due to the N-CH_3 group and a broad peak at δ 5.59 for the N-H proton. The isolation of 22 and 23 is attributed to the protonation of the initially formed addition adduct by the Et_3NH^+ cation. Protonation at nitrogen was confirmed by the IR spectra of the products which showed strong intensity N-H stretching bands at 3420 and 3470 cm^{-1} for 22 and 23, respectively. Also observed were strong intensity C-N stretching bands at 1511 cm^{-1} for 22 and 1506 cm^{-1} for 23. These values are both within the region reported previously for the C-N stretching frequency of bridging thiocarbamoyl ligands.³²

Again only one isomer was found to be present for 19, 20, 22 and 23. The ^{13}C NMR spectra of these compounds indicates the thiolate ethyl group is oriented equatorially since signals were observed at δ_{C} 35.8, 35.1, 32.6 and 35.3, respectively, attributed to the SCH_2 carbon in each compound. These compounds have a chiral framework, as do the μ -acyl complexes 3 and 6, which renders the SCH_2 protons diastereotopic. For this reason the SCH_2 protons appear as complex multiplets in the ^1H NMR spectra and the benzyl methylene protons of 19 as an AB quartet. The ^{13}C NMR spectrum of 22 showed a peak at δ_{C} 249.7 assigned to the thiocarbamoyl carbon. However, for 23 the carbamoyl carbon peak could not be located, but might be under one of the carbonyl carbon peaks.

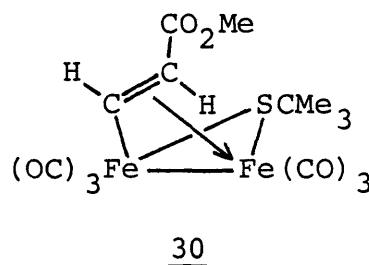
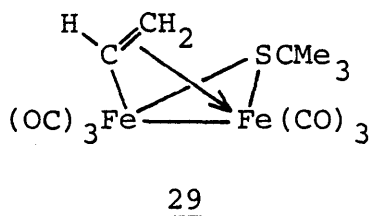
Given the success of the propargyl halide type electrophiles to react with the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system via apparent attack at the alkyne function, one might wonder whether acetylenes in general would also be suitable reactants. The substitution of a carbonyl ligand in the diiron anion complex, $[\text{10}]^- [\text{Et}_3\text{NH}]^+$, with an acetylene was envisioned as potentially leading to a bridging acetylene complex, 24, (eq.11). The first attempted reaction of this type involved addition of phenylacetylene to the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ mixture at room temperature. The course of the reaction was monitored by TLC which showed the formation of a product as the solution became dark red. After a reaction period of 42 h, the solvent was removed followed by filtration chromatography (silicic acid/pentane) of the remaining red oil. A dark red solid was isolated in



65% yield which proved not to be 24. Instead, as in the formation of 22 and 23, the $[\text{Et}_3\text{NH}]^+$ cation had provided a proton by which a $(\mu\text{-vinyl})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ complex was produced. The ^1H NMR spectrum of this product, however, revealed that two isomers, 25 and 26, which had not been resolved by chromatography were present in the recrystallized sample in 2/1 (25/26) ratio. The ratio could be determined by integration of the distinctive vinyl proton resonance for each in the ^1H NMR spectrum (Table 5). Adding phenylacetylene to the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{H}$ system also led to the isolation of two isomers analogous to 25 and 26 in 23% yield after a reaction time of 49 h. These two compounds existed as a 1.6/1 (27/28) mixture in the



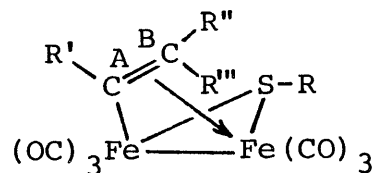
recrystallized sample, mp 85-90°C. Given the low yield obtained in this reaction, it was repeated at reflux for 1 h followed by stirring at room temperature for an additional 4 h. This did lead to an improved yield of 49%, and again both isomers were obtained, 1.4/1 (27/28). Acetylene also reacted with the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ system to give the simple σ, π bridging vinyl complex. $(\mu\text{-H}_2\text{C=CH})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$, 29, after the solution was refluxed for 1 h while acetylene was bubbled into it. It was isolated in 20% yield as a dark red oil. Methyl propiolate reacted very quickly at room temperature in the same system, resulting in a dark red solution. Work-up of the reaction mixture after 2.5 h led to the isolation of 30 in 49% yield as a red oil. Unlike the phenylacetylene derivative,



only one isomer, 30, was observed by ^1H and ^{13}C NMR spectroscopy.

The stereochemistry of the vinyl ligands has been assigned based on ^1H NMR data. In the ^1H NMR spectrum of the simple derivative 29, the shift of the C_A proton occurs at low field, δ 7.77, as a doublet of doublets ($J_{\text{trans}} = 13.9$, $J_{\text{cis}} = 9.2\text{Hz}$) being coupled to both the cis and trans C_B protons (Table 4). This harmonizes with the ^1H NMR data reported by King for other

Table 5. ^1H NMR Data for $(\mu\text{-vinyl})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ Complexes.

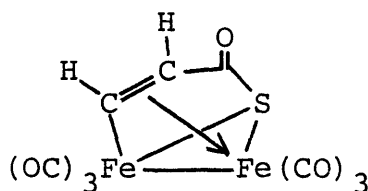


R	$\begin{array}{c} \text{R}' \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}'' \end{array}$	$\delta_{\text{H}} \text{ R}'$	$\delta_{\text{H}} \text{ R}''$	$\delta_{\text{H}} \text{ R}''$
Me_3C	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$	7.77 (dd, $J = 13.9\text{Hz}, 9.2\text{Hz}$)	3.35 (d, $J = 9.2\text{Hz}$)	3.08 (d, $J = 13.9\text{Hz}$)
Me_3C	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$		3.58 (d, $J = 2.5\text{Hz}$)	2.79 (d, $J = 2.5\text{Hz}$)
Et	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$		3.60 (d, $J = 2.5\text{Hz}$)	2.42 (d, $J = 2.5\text{Hz}$)
Me_3C	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \text{CO}_2\text{Me}$	8.83 (d, $J = 12.2\text{Hz}$)		3.45 (d, $J = 12.2\text{Hz}$)

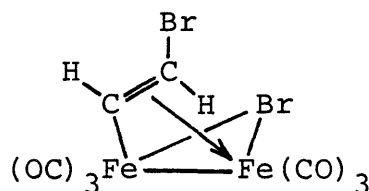
Table 5 (Con't)

R	$\begin{array}{c} \text{R}' \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}'' \end{array}$	$\delta_{\text{H}} \text{ R}'$	$\delta_{\text{H}} \text{ R}''$	$\delta_{\text{H}} \text{ R}'''$
Me_3C	$\begin{array}{c} \text{H} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	8.30 (d, J = 13.7Hz)		4.68 (d, J = 13.7Hz)
Et	$\begin{array}{c} \text{H} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	8.50 (d, J = 13.7Hz)		4.40 (d, J = 13.7Hz)
Me_3C	$\begin{array}{c} \text{Et} \quad \text{Et} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$			3.19
Et	$\begin{array}{c} \text{Et} \quad \text{Et} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$			2.84

$(\mu\text{-H}_2\text{C=CH})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ complexes.⁹ In two μ -vinyl- $\text{Fe}_2(\text{CO})_6$ complexes, 31 and 32, for which the stereochemistry of the



31



32

vinyl ligands has been determined by X-ray diffraction, cis and trans coupling constants of $J_{\text{cis}} = 6.7\text{Hz}$ and $J_{\text{trans}} = 10.5\text{Hz}$ have been reported.^{27,33} From these representative values in which the trans coupling is larger than the cis coupling, the assignments of coupling constants in 29 were made. The peak at δ 3.08 ($J = 13.9\text{Hz}$) results from the proton trans to the C_A proton and the peak at δ 3.35 ($J = 9.2\text{Hz}$) from the cis proton. The complexes 25, 27 and 30 have vinyl proton coupling constants of 13.7, 13.7 and 12.2Hz, respectively, attributed to a trans configuration of the vinyl protons. For compounds 26 and 28 the absence of a low field vinyl proton signal in their ^1H NMR spectra indicates that their vinyl protons are both attached to C_B . Both spectra consist of two doublets with small geminal coupling constants of 2.5Hz. For these two compounds the signal which appears at lower field is attributed to the proton cis to the C_A substituent in harmony with the relative shift positions found for the vinyl protons of 29 (Table 5).

The ^{13}C NMR data for these new μ -vinyl compounds indicate

that the C_A carbons are deshielded with respect to the C_B carbons (Table 6). For 26 and 28 the observation of a doublet of doublets in the proton coupled spectra for the C_B carbons confirms that two hydrogen atoms are attached to this carbon as indicated by the 1H NMR spectra.

The addition of 3-hexyne to the $Fe_3(CO)_{12}/EtSH/Et_3N$ system led to the isolation of two products, both of which contained a hexenyl ligand. The reaction mixture initially was stirred at room temperature for 20 h, but TLC analysis of this solution showed little product formation. The solution then was refluxed for 20 min prior to the standard work up of the reaction mixture. Separation of the two products formed was accomplished by filtration chromatography (silicic acid/pentane). Both were red solids. The first to elute from the column was the expected μ -3-hexenyl complex 31 isolated in 51% yield, (eq.12). The mass

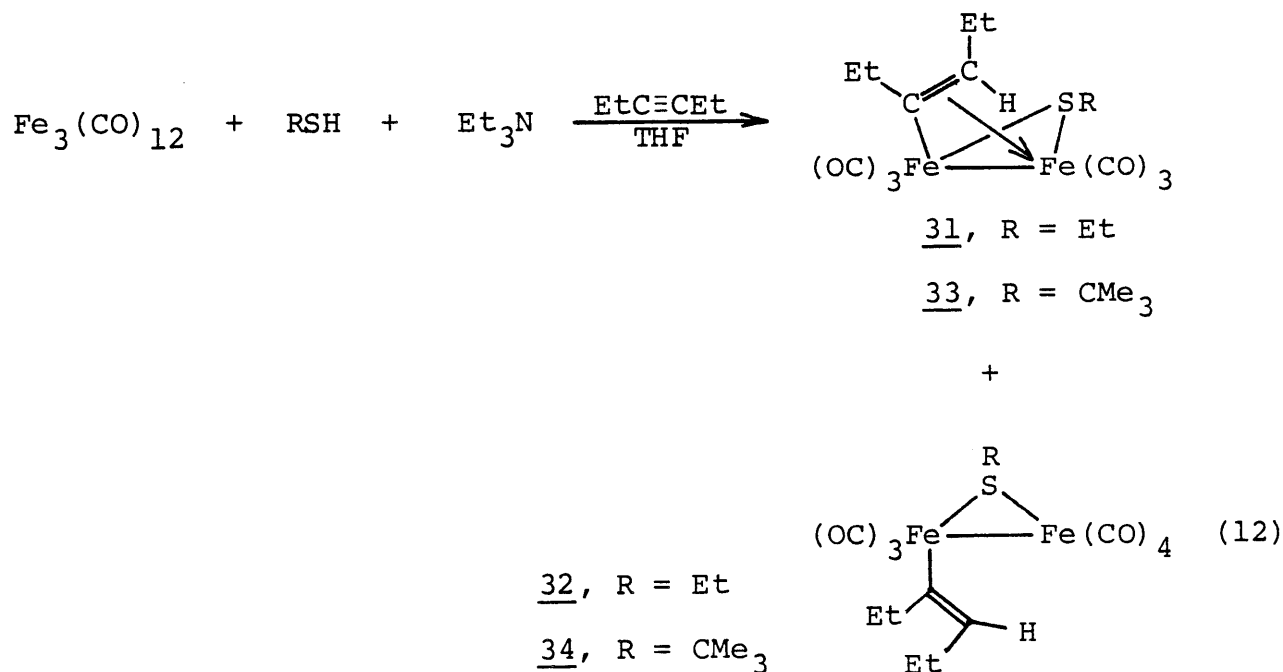
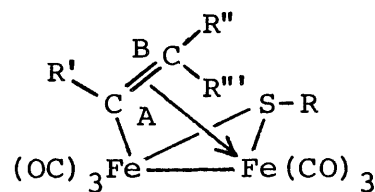


Table 6. ^{13}C NMR Data for $(\mu\text{-vinyl})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ Complexes.



R	$\begin{array}{c} \text{R}' \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}'' \end{array}$	δ_{C_A}	δ_{C_B}
Me_3C	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$	154.8 (d, J = 151Hz)	74.8 (dd, J = 163, 157Hz)
Me_3C	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$	185.0	68.8 (dd, J = 155, 163Hz)
Et	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$	187.4	67.1 (dd, J = 156, 162Hz)
Me_3C	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{CO}_2\text{Me} \end{array}$	161.3 (d, J = 154Hz)	76.0 (d, J = 166Hz)

Table 6. (Con't)

R	$\begin{array}{c} \text{R}' \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{R}'' \end{array}$	δ_{C_A}	δ_{C_B}
Me_3C	$\begin{array}{c} \text{H} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	141.5 (d, J = 145Hz)	96.6 (d, J = 158Hz)
Et	$\begin{array}{c} \text{H} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	144.2 (d, J = 149Hz)	95.2 (d, J = 159Hz)
Me_3C	$\begin{array}{c} \text{Et} \quad \text{Et} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	180.8	100.1 (d, J = 156Hz)
Et	$\begin{array}{c} \text{Et} \quad \text{Et} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	183.3	99.7 (d, J = 161Hz)

spectrum and combustion analysis of 31 confirmed that it was the diiron hexacarbonyl complex. Table 6 reports the expected low field singlet (δ_C 183.3) of C_A and the doublet (δ_C 97.7, $J = 161\text{Hz}$) of C_B at higher field found in the ^{13}C NMR spectrum. The other product isolated from this reaction, however, was a mixture of two isomers in a ratio of 4.5/1. The ratio was determined by integration of the two triplets in the vinyl proton region of the ^1H NMR spectrum. The ^{13}C NMR spectrum also revealed the presence of two isomers with four signals attributed to vinyl carbons (Table 7). These vinyl carbons, however, are clustered around δ_C 153 unlike the μ -vinyl ligands for which two signals are observed separated by 45 to 120 ppm (Table 6). In the IR spectrum of this material a band at 1629 cm^{-1} was found which was assigned to a $\nu(\text{C}=\text{C})$ of the vinyl ligand. Such absorption bands are not observed for the μ -vinyl ligands due to coordination of the carbon-carbon double bond to the iron atom. These spectroscopic data indicated that the complex 32, a diiron-heptacarbonyl compound containing a μ -vinyl ligand, had been isolated, eq.12. This conclusion was also supported by the combustion analysis and mass spectrum which contained peaks for the parent ion and successive loss of seven carbonyl ligands.

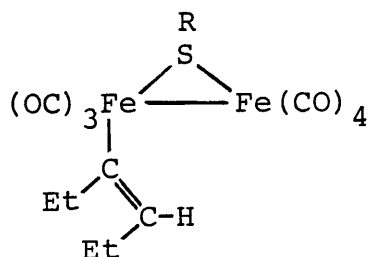
When 3-hexyne was allowed to react with the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ system at reflux for 0.5 h followed by stirring at room temperature for 5 h, both the μ -vinyl complex (33, 35% yield) and σ -vinyl complex (34, 25% yield) were isolated, eq.12. The two compounds were separated by column chromatography

(silicic acid/pentane); 33 was obtained as a red solid, mp 65-67°C, and 34 as a red oil. Two isomers of 34 in a ratio of 1.2/1 were observed by ^1H and ^{13}C NMR spectroscopy indicating that it was structurally analogous to 32, Table 7. A $\nu(\text{C}=\text{C})$ band at 1631 cm^{-1} in the IR spectrum confirmed the presence of a σ -vinyl ligand.

The structures of the geometric isomers of 32 and 34 could not be determined with certainty. It could be that the isomers are the result of cis/trans isomerism at the C=C bond. Although only one isomer of the μ -hexenyl complexes, 31 and 33, was formed and has been assigned the structure with the vinyl ethyl groups cis to one another. On the other hand, the isomers of 32 and 34 could be explained in terms of the vinyl ligand occupying different coordination sites on the iron atom rather than in terms of cis/trans isomerism at the C=C bond. Since the SFe_2 unit defines a three-membered ring, another possibility is that isomers are the result of the alkyl group on the sulfur atom being oriented on the same or on the other side of the ring system with respect of the σ -vinyl ligand.

Although the addition of phenylacetylene was not regio-specific, in that protonation occurred at both alkyne carbons, as far as can be determined overall addition of the iron-proton unit occurs in a cis fashion. This is evident in the formation of 25, 27 and 30 in which the stereochemistry of the μ -vinyl ligands was determined. For the other μ -vinyl complexes whether or not the iron and proton functions were added to the same side of the $\text{C}\equiv\text{C}$ bond cannot be ascertained from any spectroscopic

Table 7. NMR Data for



<u>R</u>	<u>δ vinyl proton</u>	<u>δ_C Fe-C</u>	<u>$\delta_C = CH$</u>
Et	6.48 (maj) ^a	151.2 (min)	153.9 (d, J = 152Hz, maj)
	6.65 (min)	151.7 (maj)	155.5 (d, J = 156Hz, min)
Me ₃ C	6.51 (maj)	150.8 (min)	154.7 (d, J = 156Hz, maj)
	6.78 (min)	151.8 (maj)	155.6 (d, J = 157Hz, min)

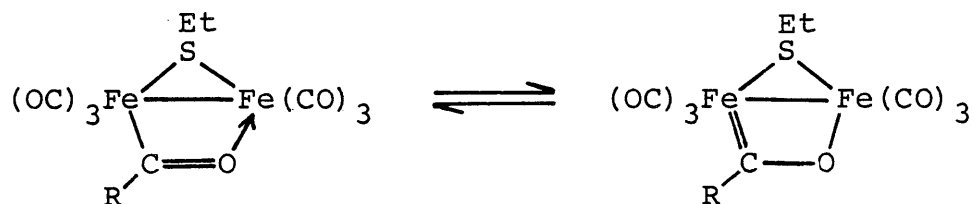
^aMaj refers to the more abundant isomer, min to the other.

data, although as indicated by the formation of 25, 27 and 30 cis addition would appear to be likely. For this reason, the isomers of 32 and 34 probably are not the result of cis/trans orientations of the vinyl ethyl groups since this would necessitate both cis and trans additions to the alkyne function. The isolation of 32 and 34 may also indicate that the σ -vinyl heptacarbonyl complexes are intermediates in the addition of acetylenes to $[\underline{10}]^- [\text{Et}_3\text{NH}]^+$. The formation of the μ -vinyl hexacarbonyl complexes then could occur by intramolecular carbonyl substitution with bridging of the vinyl ligand.

In this initial study of the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system convenient syntheses of thiolate-bridged diiron hexacarbonyl complexes with bridging acyl, allyl, allenyl, dithioester, carbamoyl, thiocarbamoyl and vinyl ligands have been discovered. These reactions have extended greatly the number and type of $(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6$ complexes available for study and have provided a superior route to these complexes over the existing synthetic methods. Armed with this new synthetic method, it is of interest to study the reaction chemistry of some of these dinuclear compounds since they are now readily available. In this respect, the acyl complexes 3 and 6 have been investigated. Although a number of μ -acyl complexes have been reported, the reaction chemistry of these compounds, especially that associated with the μ -acyl ligand, has received little attention.^{30,34} This is in contrast to the mononuclear acyl compounds which recently have attracted much attention.³⁵

The bridging acyl ligands of 3 and 6 can be thought of in

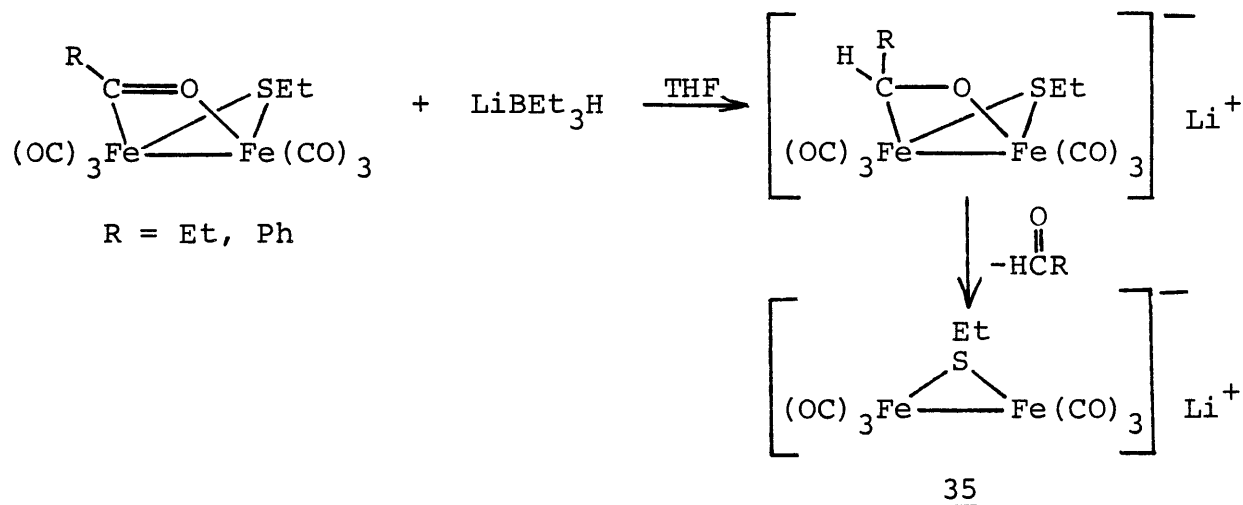
terms of two resonance forms, the acyl ligand and an oxycarbene form, Scheme 4. Both forms predict that the acyl carbon could



Scheme 4

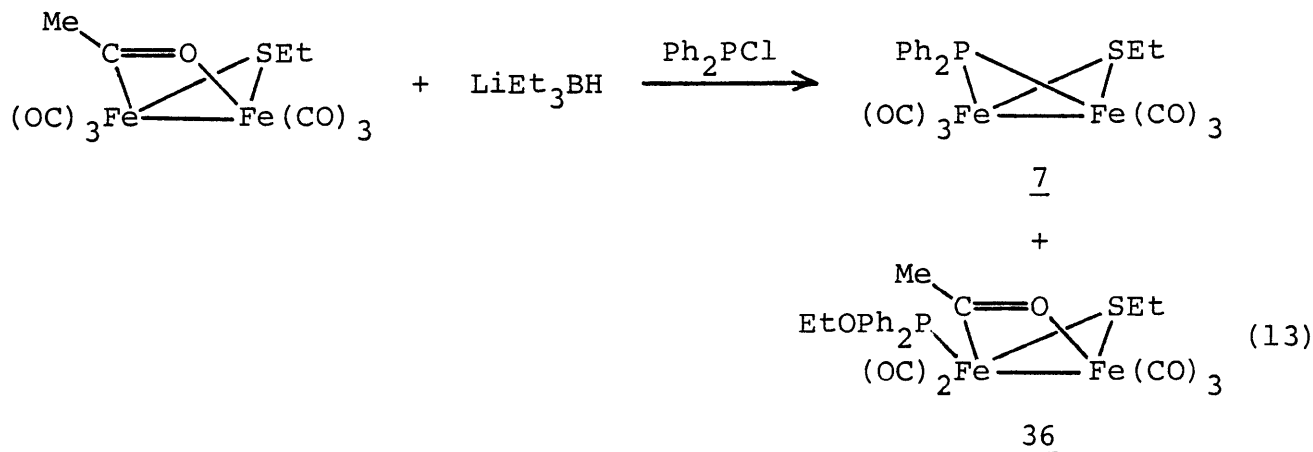
be susceptible to nucleophilic attack; the acyl ligand as a metallo-ketone coordinated to a Lewis acid center and Fischer type carbenes are well known to be electrophilic.³⁶ With this in mind, it was felt that the addition of LiEt_3H to 3 or 6 could result in nucleophilic attack of the hydride at the acyl carbon to generate the corresponding aldehyde. Liberation of the aldehyde would leave the anionic $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]^-$ species, 35, which could be used as a reagent in further synthetic applications, Scheme 5. Anion 35 is very similar to the anionic species, 10, postulated as the reactive agent in the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system, differing only by the absence of the bridging carbonyl ligand. As such, 35 would be a coordinatively unsaturated anionic species which might make it potentially more reactive and less stable than 10.

With these concepts in mind, a red THF solution of 3 (2.21 mmol) was cooled to -78°C , whereupon LiEt_3H (2.21 mmol, Super-Hydride, Aldrich) was added. The solution immediately became brown and was stirred for 30 min. An equivalent of



Scheme 5

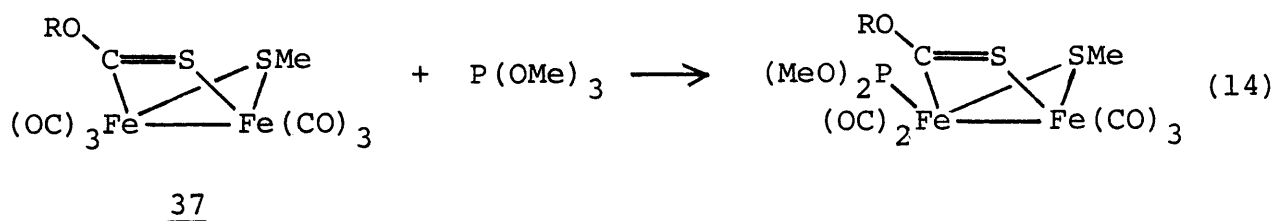
diphenylchlorophosphine was added and the solution was allowed to warm to room temperature. After a reaction period of 20 h, two products were isolated by chromatography (silicic acid). The first to elute from the column was the expected product, $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$, isolated in 55% yield. The second product, obtained as a dark red oil in 32% yield, was identified as $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_5\text{PPh}_2\text{OEt}$, 36, (eq.13). The



isolation of these two products confirmed the success of this synthetic method and also revealed the fate of the acetyl ligand and added hydride. The reaction between 3 and LiEt_3H apparently proceeded as outlined in Scheme 5, but the liberated aldehyde did not remain an innocent by-product. As it was formed, the acetaldehyde competed with 3 as an electrophile, reacting with LiEt_3H to form lithium ethoxide. This diversion of the hydride to a new reactant prevented complete conversion of 3 to the anion 35 resulting in only a 55% yield of 7. However, the unreacted starting material 3 was not reisolated. Instead the new μ -acetyl complex 36 was obtained in 32% yield, formed from a carbonyl substitution reaction of 3 with Ph_2POEt . The ethoxyphosphine was formed in-situ in the reaction between the generated lithium ethoxide and remaining diphenylchlorophosphine. The isolation of 7 and 36 accounted for 87% of the starting material 3, with 64% of the added hydride contained in the ethoxy group of 36.

The identification of 36 was confirmed by spectral data and the combustion analysis. The ^{13}C NMR spectrum contained a peak at δ_{C} 300.3 resulting from the μ -acyl carbon which falls within the region, δ_{C} 289.0 to 301.9, found for the acyl carbons of the related hexacarbonyl complexes 3 and 6. In the ^1H NMR spectrum the OCH_2 and SCH_2 protons appear as complex multiplets at δ 3.92 and 2.16, respectively, resulting from diastereotopic methylene protons. This is due to the chiral framework of the molecule which is also a characteristic of 3 and 6. Only one isomer of 36 was observed by NMR spectroscopy

with the thiolate ethyl group in the equatorial position, δ_C 32.0 for the SCH_2 carbon. The Ph_2POEt ligand is probably located on the iron atom to which the acetyl-carbon is bound. This is in harmony with results reported by Patin et al for the related thiocarbonyl bound complexes 37 for which carbonyl substitution occurs first at the iron atom bound to the thio-carbonyl carbon, (eq.14).³⁷



Since two competitive reactions occurred when $LiEt_3H$ was added to 3, hydride addition to 3 and to acetaldehyde, the use of two equivalents of $LiEt_3H$ was necessary to allow both processes to go to completion. Thus, two equivalents of $LiEt_3H$ was added to 3 in THF at $-78^\circ C$, after stirring for 20 min an excess of allyl chloride was added. The solution immediately became red and after stirring an additional 2 h at room temperature, 13 was isolated in 82% yield. In the same manner $(\mu-H_2C=C=CH)(\mu-EtS)Fe_2(CO)_6$, 15, was isolated in 56% yield when propargyl bromide was added to the $2LiEt_3H/3$ reaction mixture.

This reaction method for replacing a μ -acyl ligand with another three-electron donor bridging ligand could also be accomplished with $(\mu-PhCO)(\mu-EtS)Fe_2(CO)_6$, 6. The reaction between 6 and two equivalents of $LiEt_3H$ in THF at $-78^\circ C$

resulted in a brown solution. Addition of Ph_2PCl to this solution allowed the isolation of $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ in 85% yield. Following the same procedure and using allyl chloride as the electrophile resulted in the isolation of 13 in 82% yield. These two reactions indicate that 6 interacts with LiEt_3H as 3 does to form anion 35. The stability of 35 at temperatures above -78°C appears to be limited, however. When a solution of 35, generated from 6 and two equivalents of LiEt_3H , was removed from the -78°C cold bath and stirred for 1 h prior to the addition of Ph_2PCl , the yield of $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ was reduced to 33%.

This particular synthetic method for making $(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6$ type complexes, at this point, is not as convenient as using the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system. However, as studies of both these synthetic methods continue, their differences and specialized uses will become more apparent.

Experimental Section

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone ketyl. Carbon disulfide was distilled from phosphorus pentoxide. Reagent grade pentane, dichloromethane, ethanol and methanol were deoxygenated by bubbling nitrogen through them for 15 min prior to use. 3-Bromo-3-methyl-1-propyne was synthesized according to a literature method.³⁸ 1-Chloro-2-pentyne was prepared via the chlorination of 2-pentynol following the procedure outlined in ref.39. Triiron dodecacarbonyl was prepared by a literature method.⁴⁰ Ethanethiol and t-butanethiol were deoxygenated by bubbling nitrogen through them for 15 min and used as obtained.

Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 ml) in a 350 ml glass-frit filter funnel, was used in most cases. Column chromatography was performed with a 350 x 25 mm column using silicic acid. All chromatography was done without exclusion of atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at -20°C.

Infrared spectra were obtained using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JeolFX-90Q or a Bruker 250 NMR spectrometer operating at 90MHz and 250MHz, respectively. ¹³C NMR spectra were obtained using a JeolFX-90Q or Bruker

270 NMR instrument operating at 22.5MHz and 67.9MHz, respectively. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained using a JeolFX-90Q instrument operating at 36.2MHz referencing to external 85% aqueous H_3PO_4 set at $\delta_{\text{P}}0$. Mass spectra were obtained with a Finnigan-3200 spectrometer operation at 70eV. Melting points were determined on a Büchi Melting Point Apparatus using analytically pure samples and are uncorrected. Microanalyses were preformed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Crystallography

Compound 13 crystallizes in the space group $\text{Pn}2_1\text{a}$. Data in the range $3^\circ < 2\theta < 55^\circ$ (+h, +k, +l) were collected using $\text{MoK}\alpha$ radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection and reduction procedures have been described in detail elsewhere.⁴² The structure was solved by direct-methods using MULTAN78 and refined by full-matrix least-squares techniques using SHELX-76. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the ethyl group were placed in calculated positions ($\text{C-H} = 0.95\text{\AA}$; $\text{H-C-H} = 109.5^\circ$) and were constrained to ride on the carbon atom to which they are bonded. Hydrogen atoms of the allyl group were located in a difference Fourier map and were included in the refinement as invariants with $U = 0.10\text{\AA}^2$. Final residual indices are $R_1 = 0.034$ and $R_2 = 0.037$ for 1469 observed reflections [$F_0 > 4\sigma(F_0)$] and 185 variables.

Data in the range $3^\circ < 2\theta < 55^\circ$ ($\pm h$, $\pm k$, $\pm l$) were collected for compound 16, space group $P\bar{1}$, using $\text{MoK}\alpha$ radiation.⁴² All nonhydrogen atoms were refined anisotropically. Hydrogen atoms of the t-butyl group were placed in calculated positions and were constrained to ride on the carbon atoms to which they are bound. Hydrogen atoms of the allenyl group could not be located in difference Fourier maps and have been ignored. Final residual indices are $R_1 = 0.048$ and $R_2 = 0.055$ for 2058 observed reflections [$F_o > 4\sigma(F_o)$] and 200 variables.

Table 8 Crystal Data for 13.

$a = 13.400(2) \text{ \AA}$	space group = $Pn2_1a$
$b = 6.958(1) \text{ \AA}$	$Z = 4$
$c = 15.970(2) \text{ \AA}$	mol. wt. = 381.96 g
$V = 1489.0 \text{ \AA}^3$	$\rho(\text{calcd}) = 1.704 \text{ g cm}^{-3}$
	$\mu = 20.70 \text{ cm}^{-1} \text{ }^a$

^aAbsorption correction not applied.

Table 9. Final Positional and Thermal Parameters for 13.

Atom	x	y	z	U11 or U	U22	U33	U12	U13	U23
Fe(1)	0.18677(4)	0.0000	0.16701(3)	0.0398(3)	0.0465(3)	0.0333(3)	-0.0008(5)	-0.0007(2)	0.0010(5)
Fe(2)	0.26864(4)	-0.0075(2)	0.00075(3)	0.0495(3)	0.0528(4)	0.0325(3)	-0.0007(6)	0.0000(3)	0.0031(4)
S	0.26187(8)	0.2424(3)	0.09021(7)	0.0444(6)	0.0442(6)	0.0458(8)	-0.0015(6)	-0.0052(5)	0.0044(6)
C(1)	0.3862(4)	0.2971(10)	0.1299(4)	0.053(3)	0.063(4)	0.075(3)	-0.017(3)	-0.009(3)	0.000(3)
C(2)	0.3797(7)	0.3994(13)	0.2133(5)	0.084(5)	0.084(5)	0.125(7)	-0.002(4)	-0.034(5)	-0.044(5)
C(3)	0.0534(4)	0.1082(9)	0.1035(3)	0.044(2)	0.074(4)	0.051(3)	0.003(3)	-0.009(2)	0.008(3)
C(4)	0.0792(3)	0.0202(12)	0.0258(3)	0.0381(20)	0.069(4)	0.058(2)	-0.007(3)	-0.0168(19)	0.008(4)
C(5)	0.1220(4)	0.1129(10)	-0.0443(3)	0.053(3)	0.080(4)	0.048(3)	0.000(3)	-0.010(2)	0.004(3)
C(11)	0.2991(4)	-0.0777(8)	0.2070(3)	0.055(3)	0.047(3)	0.045(3)	0.008(2)	0.001(2)	0.000(2)
O(11)	0.3676(4)	-0.1208(7)	0.2445(3)	0.073(3)	0.077(3)	0.084(3)	0.017(3)	-0.028(2)	0.001(3)
C(12)	0.1398(4)	0.1140(10)	0.2489(3)	0.048(3)	0.072(4)	0.049(3)	0.008(3)	0.000(2)	-0.007(3)
O(12)	0.1094(3)	0.1861(10)	0.3066(3)	0.080(3)	0.135(5)	0.062(2)	0.025(3)	0.007(2)	-0.031(3)
C(13)	0.1298(4)	-0.2340(9)	0.1654(3)	0.054(3)	0.061(4)	0.044(2)	-0.012(3)	0.001(2)	0.003(3)
O(13)	0.0940(4)	-0.3797(7)	0.1704(3)	0.087(3)	0.068(3)	0.080(3)	-0.027(3)	-0.006(2)	0.009(3)
C(21)	0.3713(5)	-0.1113(10)	0.0384(3)	0.070(4)	0.081(4)	0.045(3)	0.022(3)	0.000(3)	-0.008(3)
O(21)	0.4448(4)	-0.1812(11)	0.0563(3)	0.087(3)	0.143(5)	0.087(3)	0.051(4)	-0.013(3)	-0.015(4)
C(22)	0.3115(4)	0.1056(11)	-0.0879(4)	0.065(3)	0.080(4)	0.047(3)	-0.013(3)	-0.002(3)	0.006(3)
O(22)	0.3441(4)	0.1842(10)	-0.1450(3)	0.128(4)	0.128(5)	0.061(3)	-0.029(4)	0.015(3)	0.037(3)
C(23)	0.2258(4)	-0.2345(10)	-0.0426(3)	0.070(3)	0.061(4)	0.046(3)	0.000(3)	0.005(2)	-0.001(3)
O(23)	0.2052(4)	-0.3810(8)	-0.0714(3)	0.110(3)	0.069(3)	0.088(4)	-0.009(3)	0.004(3)	-0.016(3)
H(11)	0.4209(4)	0.3759(10)	0.0910(4)	0.085(16)					
H(12)	0.4219(4)	0.1804(10)	0.1377(4)	0.085(16)					
H(21)	0.4437(7)	0.4478(13)	0.2281(5)	0.15(2)					
H(22)	0.3588(7)	0.3080(13)	0.2539(5)	0.15(2)					
H(23)	0.3332(7)	0.5024(13)	0.2114(5)	0.15(2)					
H(31)	-0.0034	0.0001	0.1355	0.10					
H(32)	0.0506	0.2609	0.0983	0.10					
H(41)	0.0550	-0.1100	0.0181	0.10					
H(51)	0.1073	0.0115	-0.1073	0.10					
H(52)	0.1266	0.2655	-0.0391	0.10					

Numbers in parentheses are errors in the last significant digit(s).
The anisotropic temperature factors are of the form
 $\text{EXP}(-2\pi^2(U_{11}H^2+2U_{12}H+U_{22}K^2+2U_{13}HK+2U_{23}H+U_{33}K^2+U_{12}HK+U_{13}HK+U_{23}HK+BSTAR+...))$

Table 10 Crystal Data for 16.

$a = 8.455(1) \text{ \AA}$	$V = 848.9 \text{ \AA}^3$
$b = 9.478(1) \text{ \AA}$	space group = $P\bar{1}$
$c = 10.926(2) \text{ \AA}$	$Z = 2$
$\alpha = 90.95(1)^\circ$	mol. wt. = 407.99g
$\beta = 97.44(1)^\circ$	$\rho(\text{calcd.}) = 1.596 \text{ g cm}^{-3}$
$\gamma = 101.81(1)^\circ$	$\mu = 18.18 \text{ cm}^{-1} \text{ }^a$

^aAbsorption correction not applied.

atom	x	y	z	U11 or U	U22	U33	U12	U13	U23
Fe(1)	0.66290(11)	0.73388(9)	0.33808(8)	0.0422(6)	0.0478(6)	0.0389(5)	0.0146(5)	0.0114(4)	0.0002(4)
Fe(2)	0.95221(11)	0.74811(10)	0.28870(8)	0.0398(6)	0.0467(6)	0.0511(6)	0.0124(5)	0.0095(5)	0.0030(4)
S	0.72078(19)	0.67004(16)	0.15235(14)	0.0448(9)	0.0404(8)	0.0366(8)	0.0141(7)	0.0102(7)	0.0039(6)
C(11)	0.5706(10)	0.8816(8)	0.2898(6)	0.076(5)	0.069(5)	0.050(4)	0.031(4)	0.024(4)	0.002(4)
O(11)	0.5058(8)	0.9746(6)	0.2628(5)	0.139(6)	0.107(5)	0.090(4)	0.044(4)	0.088(5)	0.031(4)
C(12)	0.4821(9)	0.6012(8)	0.3422(6)	0.059(5)	0.077(5)	0.044(4)	0.020(4)	0.020(4)	0.015(4)
O(12)	0.3697(7)	0.5130(7)	0.3480(5)	0.068(4)	0.112(5)	0.085(4)	-0.019(4)	0.026(3)	0.002(3)
C(13)	0.6798(9)	0.7989(8)	0.4948(7)	0.059(5)	0.066(5)	0.056(5)	0.020(4)	0.013(4)	-0.002(4)
O(13)	0.6880(8)	0.8404(6)	0.5943(5)	0.117(5)	0.109(5)	0.054(4)	0.031(4)	0.014(3)	-0.021(3)
C(21)	0.9514(9)	0.9350(8)	0.2892(7)	0.060(5)	0.055(5)	0.081(6)	0.009(4)	0.003(4)	0.004(4)
O(21)	0.9618(7)	1.0585(6)	0.2934(6)	0.093(5)	0.051(3)	0.145(6)	0.011(3)	-0.004(4)	-0.010(4)
C(22)	1.0799(9)	0.7149(9)	0.1777(8)	0.049(5)	0.083(6)	0.079(6)	0.016(4)	0.027(4)	0.015(4)
O(22)	1.1650(8)	0.6862(7)	0.1064(6)	0.086(5)	0.153(6)	0.114(5)	0.040(4)	0.064(4)	0.011(4)
C(23)	1.1132(9)	0.7804(8)	0.4120(7)	0.051(5)	0.082(6)	0.064(5)	0.014(4)	0.003(4)	0.002(4)
O(23)	1.2234(8)	0.8026(7)	0.4883(6)	0.076(4)	0.119(5)	0.089(5)	0.006(4)	-0.016(4)	0.004(4)
C(1)	0.6811(8)	0.7747(7)	0.0125(6)	0.056(4)	0.053(4)	0.040(4)	0.015(3)	0.009(3)	0.008(3)
C(2)	0.7521(10)	0.9347(7)	0.0254(7)	0.078(5)	0.059(5)	0.071(5)	0.013(4)	0.013(4)	0.024(4)
C(3)	0.4959(9)	0.7402(8)	-0.0217(7)	0.065(5)	0.088(6)	0.067(5)	0.013(5)	-0.014(4)	0.014(4)
C(4)	0.7586(11)	0.7045(9)	-0.0850(7)	0.130(8)	0.115(7)	0.051(5)	0.057(6)	0.042(5)	0.017(5)
C(5)	0.8135(8)	0.6074(6)	0.3986(6)	0.053(4)	0.041(4)	0.061(4)	0.014(3)	0.025(4)	0.008(3)
C(6)	0.8798(8)	0.5258(7)	0.3235(6)	0.055(4)	0.055(4)	0.056(4)	0.022(4)	0.008(3)	0.022(3)
C(7)	0.9075(11)	0.4052(8)	0.2737(7)	0.098(6)	0.054(4)	0.077(6)	0.041(5)	0.008(5)	0.008(4)
H(21)	0.7035(10)	0.9774(7)	0.0861(7)	0.117(11)					
H(22)	0.7310(10)	0.9771(7)	-0.0516(7)	0.117(11)					
H(23)	0.8665(10)	0.9502(7)	0.0499(7)	0.117(11)					
H(31)	0.4475(9)	0.7836(8)	0.0387(7)	0.117(11)					
H(32)	0.4568(9)	0.6387(8)	-0.0251(7)	0.117(11)					
H(33)	0.4681(9)	0.7771(8)	-0.1002(7)	0.117(11)					
H(41)	0.7134(11)	0.6039(9)	-0.0928(7)	0.117(11)					
H(42)	0.8730(11)	0.7198(9)	-0.0607(7)	0.117(11)					
H(43)	0.7376(11)	0.7466(9)	-0.1622(7)	0.117(11)					

Numbers in parentheses are errors in the last significant digit(s).
The anisotropic temperature factors are of the form
 $\text{EXP}(-2*\pi^2(U11*H^2+2*ASTAR*H+....+2U12*H*K+ASTAR*BSTAR+....))$

Table 11 Final Positional and Thermal Parameters for 16.

Reaction Between $\text{Fe}_3(\text{CO})_{12}$, Sodium Ethanethiolate and Acetyl Chloride. (GBW-IX-38).

A 300 ml, three-necked, round-bottomed flask equipped with a stir-bar and a serum cap was charged with 0.11 g (2.80 mmol) of NaNH_2 (Alfa) and 50 ml of THF under nitrogen. Ethanethiol (Fluka), 0.25 ml (3.38 mmol), was added and the mixture stirred for 1 h to allow formation of EtSNa . Triiron dodecacarbonyl, 1.5 g (2.98 mmol), then was added as a solid against a flow of nitrogen. Gas evolution immediately was observed and the green color of the $\text{Fe}_3(\text{CO})_{12}$ discharged to produce a red-brown solution. After stirring for 1 h, 0.25 ml (3.50 mmol) of acetyl chloride (Aldrich) was added and the mixture stirred another 20 h. The solvent was removed leaving a red oil which was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected and pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.30 g (0.78 mmol, 26% yield based on $\text{Fe}_3(\text{CO})_{12}$) of a slightly air-sensitive red oil identified as a 2.2/1 (e Et/a Et) mixture of isomers of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ by comparison of its ^1H NMR spectrum to that of an authentic sample (see page 253).

Reaction Between $\text{Fe}_3(\text{CO})_{12}$, Lithium Ethanethiolate and Acetyl Chloride. (GBW-IX-49).

A 300 ml, three-necked, round-bottomed flask equipped with a stir-bar and serum caps was charged with 20 ml of THF and 0.22 ml (3.0 mmol) of ethanethiol (Fluka). This solution

was cooled to -20°C and 1.25 ml (3.0 mmol) of a 2.40M n-butyllithium solution (Alfa) was added and the solution stirred for 1 h to generate the EtSLi. Triiron dodecacarbonyl, 1.5 g (2.98 mmol), dissolved in THF was cannulated into the EtSLi solution at -20°C . The mixture became red-brown and was stirred for 1 h. Next, 0.5 ml (7.0 mmol) of acetyl chloride (Aldrich) was added and the reaction mixture removed from the cold bath and stirred for 20 h. The solvent was removed leaving a red oil which was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected and pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.41 g (1.08 mmol, 36% yield based on $\text{Fe}_3(\text{CO})_{12}$) of a slightly air-sensitive red oil identified as a 2.5/1 (e Et/a Et) mixture of isomers of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ by comparison of its ^1H NMR spectrum to that of an authentic sample (see page 253).

Reaction Between Triiron Dodecacarbonyl, Ethanethiol and Triethylamine: The Standard In-Situ Generation of $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{Et}_3\text{NH}]$.

A 300 ml, three-necked, round-bottomed flask equipped with a stir-bar and serum caps charged with 1.5 g (2.98 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and flushed with nitrogen. Tetrahydrofuran (50 ml) was added by syringe followed by the addition of 0.25 ml (3.38 mmol) of ethanethiol (Fluka) and 0.48 ml (3.50 mmol) of triethylamine (Aldrich). The solution was stirred for 15 min prior to the addition of any reactants, during which time a color change

of green to red-brown occurred.

Reaction Between Triiron Dodecacarbonyl, t-Butanethiol and Triethylamine: The Standard In-Situ Generation of $[(\mu\text{-t-Me}_3\text{CS})\text{-}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{Et}_3\text{NH}]$.

A 300 ml, three-necked, round-bottomed flask equipped with a magnetic stir-bar and serum caps was charged with 1.5 g (2.98 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and flushed with nitrogen. Tetrahydrofuran (50 ml) was added by syringe followed by the addition of 0.34 ml (3.0 mmol) of t-butyl mercaptan (Aldrich) and 0.42 ml (3.0 mmol) of triethylamine (Aldrich). The solution was stirred for 15 min prior to the addition of any reactants, during which time a color change of green to red-brown occurred.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}$ /EtSH/Et₃N Mixture and Acetyl Chloride. (GBW-X-36).

The standard $\text{Fe}_3(\text{CO})_{12}$ /EtSH/Et₃N reagent solution was prepared (p.326); to this mixture was added 0.50 ml (7.0 mmol) of acetyl chloride (Aldrich). The solution was stirred for 20 h during which time it became dark red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This was extracted with a 1/1 (v/v) mixture of pentane/ CH_2Cl_2 and filtered through a pad of silicic acid. After removal of solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which yielded 0.13 g (0.32 mmol, 11% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ as a red solid.⁴¹ Further elution with pentane/ CH_2Cl_2 (4/1, v/v) moved a red

band which gave 0.60 g (1.56 mmol, 52% yield) of $(\mu, \eta^2\text{-MeCO})\text{-}(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified as a 3/1 (e Et/a Et) mixture of isomers by its ^1H NMR spectrum (see page 253).

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Benzoyl Chloride. (GBW-IX-68).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325), to this mixture was added 0.81 ml (7.0 mmol) of benzoyl chloride (Aldrich). The solution was stirred for 23 h, during which time the solution became dark red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This oil was extracted with a 1/1 (v/v) mixture of pentane/ CH_2Cl_2 and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected, and pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which gave 1.10 g (2.47 mmol, 83% yield) of $(\mu, \eta^2\text{-PhCO})\text{-}(\mu\text{-EtS})\text{-Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 81-86°C after crystallization from pentane. It was identified as a 2.3/1 (e Et/a Et) mixture of isomers by its ^1H NMR spectrum (see page 255).

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Diphenylchlorophosphine. (GBW-IX-69).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this mixture was added 0.66 g (3.0 mmol) of Ph_2PCl (Strem). The solution was stirred for 20 h, during

which time it became dark red and a white precipitate formed. The solution was filtered and the solvent was removed leaving a red tar. This was taken up in a 4/1 (v/v) pentane/CH₂Cl₂ mixture and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted two minor yellow bands which were not collected and pentane/CH₂Cl₂ (9/1, v/v) eluted an orange band which yielded 1.26 g (2.40 mmol, 80% yield) of (μ-Ph₂P)(μ-EtS)Fe₂(CO)₆ as an orange air-stable solid, mp 111-112°C after crystallization from pentane/CH₂Cl₂. It was identified by comparison of its ³¹P {¹H} NMR spectrum to that of an authentic sample (see page 354).

Reaction Between the Standard Fe₃(CO)₁₂/Me₃CSH/Et₃N Mixture and Diphenylchlorophosphine. (GBW-X-33).

The standard Fe₃(CO)₁₂/Me₃CSH/Et₃N reagent solution was prepared (p.326); to this was added 0.66 g (3.0 mmol) of Ph₂PCl (Strem). The solution was stirred for 17 h, during which time it became dark red and a white precipitate formed. After removal of the solvent, the red tar remaining was taken up in pet ether/CH₂Cl₂ (4/1, v/v) and filtered through a pad of silicic acid. The solvent was removed from the filtrate leaving a red solid which was subjected to filtration chromatography (silicic acid/pentane). Pet ether eluted a minor yellow band which gave 0.10 g (0.22 mmol, 7% yield based on Fe₃(CO)₁₂) of (μ-Me₃CS)-Fe₂(CO)₆ as a red solid, identified by its ¹H NMR and Mass spectra. ³C Pet ether/CH₂Cl₂ (9/1, v/v) eluted an orange band which

gave 1.51 g (2.73 mmol, 91% yield) of $(\mu\text{-Ph}_2\text{P})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an orange, air-stable solid, mp 137-139°C after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3082(m), 3065(w), 2969(m), 2943(m), 2930(m), 2904(m), 2868(w), 1479(m), 1458(m), 1432(s), 1394(w), 1365(s), 1328(w), 1304(w), 1151(s), 1096(m), 1069(w), 1025(w), 999(m), 691(s), 608(s), 585(s), 520(s) cm^{-1} ;

terminal carbonyl region (pentane): 2060(s), 2021(vs), 1991(vs), 1983(vs), 1973(m) cm^{-1} .

^1H NMR (acetone- d_6 , 90MHz): δ 1.40 (s, 9H, t-butyl CH_3) and 7.2 to 7.7 (m, 5H, Ph).

^{31}P $\{^1\text{H}\}$ NMR (acetone- d_6 , 36.2MHz): δ_{P} 139.8(s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{Fe}_2\text{O}_6\text{PS}$: C, 47.69; H, 3.46%.

Found: C, 47.52; H, 3.47%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Allyl Chloride. (GBW-X-4).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325), to this was added 1.0 ml (12.2 mmol) of allyl chloride (Aldrich). The solution was stirred for 20 h, during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This was taken up in pentane and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band

which yielded 0.13 g (0.32 mmol, 11% yield based on $\text{Fe}_3(\text{CO})_{12}$ of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$.⁴¹ Further elution with pentane moved a second orange band which gave 0.91 g (2.38 mmol, 80% yield) of $(\mu\text{-CH}_2\text{CHCH}_2)(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 41-42°C after crystallization from methanol at -20°C (crystals from this source were used in the X-ray diffraction study of 12). It was identified by comparison of its ^1H NMR spectrum with that of an authentic sample (see page 355).

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}$ /EtSH/Et₃N Mixture and Propargyl Bromide. (GBW-X-12).

The standard $\text{Fe}_3(\text{CO})_{12}$ /EtSH/Et₃N reagent solution was prepared (p. 325); to this mixture was added 1.0 ml (13.3 mmol) of $\text{BrCH}_2\text{C}\equiv\text{CH}$ of propargyl bromide (Aldrich). The solution was stirred for 20 h, during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This was taken up in pentane and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Further elution with pentane moved a second orange band which yielded 1.03 g (2.71 mmol, 91% yield) of $(\mu\text{-}\eta^1, \eta^2\text{-H}_2\text{C}=\text{C}=\text{CH})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 39-41°C after crystallization from methanol. It was identified by comparison of its ^1H NMR spectrum with the of an authentic sample (see page 353).

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and Propargyl Bromide. (GBW-X-34)

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326). To this was added 1.0 ml (13.3 mmol of $\text{BrCH}_2\text{C}\equiv\text{CH}$) of propargyl bromide (Aldrich). The solution was stirred for 3.5 h, during which time it became red and a white precipitate formed. After removal of the solvent, the red oil remaining was applied to filtration chromatography (silicic acid/pet ether). Pet ether eluted a red band which gave 1.12 g (2.75 mmol, 92% yield) of $(\mu-\eta^1, \eta^2\text{-H}_2\text{C}=\text{C}=\text{CH})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, red solid, mp 56-58°C after crystallization from pentane.

IR (CHCl_3): 2970(m), 2947(m), 2930(m), 2950(w), 2868(w), 1750(m) (C=C), 1695(w), 1471(w), 1458(m), 1421(w), 1394(w), 1367(s), 1154(s), 1032(w), 1017(w), 1006(w), 890(w), 842(m), 614(s), 598(s), 496(s) cm^{-1} ;

terminal carbonyl region (pentane): 2054(s), 2040(vs), 2002(vs), 1998(vs) cm^{-1} .

^1H NMR (acetone- d_6 , 90MHz): δ 1.38 (s, 9H, t-butyl CH_3), 5.39 (d, $J = 4.4\text{Hz}$, 2H, $=\text{CH}_2$) and 7.39 (t, $J = 4.4\text{Hz}$, 1H, Fe_2CH).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 33.0 (q, $J = 129\text{MHz}$, CH_3), 48.2 (s, CMe_3), 95.5 (t, $J = 166\text{Hz}$, $=\text{CH}_2$), 113.2 (d, $J = 162\text{Hz}$, Fe_2CH), 177.7 (s, Fe-C=) and 210.2 (s, CO).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}$: C, 38.27; H, 2.96%.

Found: C, 38.20; H, 3.01%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and 3-Bromo-3-methyl-1-butyne. (GBW-X-74).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326); to this was added 1.1 g (7.5 mmol) of 3-bromo-3-methyl-1-butyne. The solution was stirred for 4.5 h, during which time it became bright red and a white precipitate formed. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 1.23 g (2.83 mmol, 95% yield) of $(\mu\text{-}\eta^1, \eta^2\text{-Me}_2\text{C}=\text{C}=\text{CH})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, red solid, mp 46-47°C after crystallization from ethanol.

IR (CHCl_3): 2983(m), 2939(m), 2918(m), 2873(m), 1755(w) $\nu(\text{C}=\text{C})$, 1462(m), 1400(w), 1371(s), 1159(s), 1022(w), 999(m), 879(m), 642(m), 605(s), 564(s), 500(s) cm^{-1} ;

terminal carbonyl region (pentane): 2072(s), 2039(vs), 2000(vs), 1993(sh) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.34 (s, 9H, t-butyl CH_3), 1.96 (s, 6H, $=\text{CCH}_3$), 7.36 (s, 1H, Fe_2CH).

^{13}C NMR (C_6D_6 , 22.5MHz): δ_{C} 25.7 (q, $J = 128\text{Hz}$, $=\text{CCH}_3$), 32.7 (q, $J = 127\text{Hz}$, t-butyl CH_3), 47.4 (s, CMe_3), 115.4 (s, $=\text{CMe}_2$), 119.6 (d, $J = 161\text{Hz}$, Fe_2CH), 171.8 (s, $\text{C}=\text{CMe}_2$) and 211.0 (s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{Fe}_2\text{O}_6\text{S}$: C, 41.32; H, 3.70%.

Found: C, 41.10; H, 3.77%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and 1-Chloro-2-pentyne. (GBW-XI-7).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326). To this was added 0.35 g (3.41 mmol) of 1-chloro-2-pentyne. The solution was stirred for 4 h; during which time the solution became red and a white precipitate formed. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 1.01 g (2.31 mmol, 77% yield) of $(\mu-\eta^1, \eta^2\text{-H}_2\text{C}=\text{C}=\text{CEt})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 54-56°C after crystallization from ethanol.

IR (CHCl_3): 2977(s), 2937(m), 2907(m), 2876(m), 1731(w), 1695(w), 1457(m), 1428(w), 1396(w), 1367(m), 1154(s), 1088(w), 1040(w), 1016(m), 971(w), 891(m), 843(m), 631(s), 570(vs), 493(s) cm^{-1} ;

terminal carbonyl region (pentane): 2063(s), 2034(vs), 1994(vs), 1986(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.26 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 1.36 (s, 9H, Me_3C), 2.55 (broad, 2H, CH_2) and 5.20 (broad, 2H, $=\text{CH}_2$).

^{13}C NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 16.8 (q, $J = 128\text{Hz}$, CH_3), 33.4 (q, $J = 127\text{Hz}$, t-butyl CH_3), 45.0 (t, $J = 132\text{Hz}$, CH_2), 49.3 (s, CMe_3), 94.7 (t, $J = 163\text{Hz}$, $=\text{CH}_2$), 148.6 (s, Fe_2CEt), 177.1 (s, FeC=) and 210.6 (s, CO).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{Fe}_2\text{O}_6\text{S}$: C, 41.32; H, 3.70%.

Found: C, 41.15; H, 3.87%.

Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and 1-Bromo-2-propanone. (GBW-X-9).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 1.37 g (10.0 mmol) of 1-bromo-2-propanone and the mixture was stirred for 24 h. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted two orange bands which gave 0.21 g (0.52 mmol, 18% yield) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ as a red solid, isolated as a 2/1 (e,a/e,e) mixture of geometric isomers. The product was identified and the isomer ratio determined by its ^1H NMR spectrum.⁴¹

Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and 1-Bromo-2-propanone at Reflux. (GBW-X-31).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this mixture was added 0.69 g (5.0 mmol) of 1-bromo-2-propanone and the solution was refluxed for 1 h. Stirring was continued an additional 30 min as the solution cooled. Removal of the solvent left a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted an orange band which gave 0.52 g (1.29 mmol, 43% yield based on $\text{Fe}_3(\text{CO})_{12}$) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison of its ^1H NMR spectrum to that of an authentic sample.⁴¹ An isomer ratio of 2/1 (e,a/e,e) was determined by integration of the ^1H NMR spectrum.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture, Carbon Disulfide and Benzyl Chloride. (GBW-X-11).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 1.0 ml (8.7 mmol) of benzyl chloride (Aldrich). The solution was stirred at room temperature for 4 h, but TLC analysis of the mixture showed no product formation. At this point 0.5 ml (8.0 mmol) of carbon disulfide (MCB) was added. The solution was stirred for 20 h during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which gave 1.42 g (2.79 mmol, 94% yield) of $(\mu\text{-PhCH}_2\text{SCS})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red, air-stable solid, mp $83\text{-}85^\circ\text{C}$ after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3004(m), 2979(m), 2942(m), 1606(w), 1502(m), 1458(m), 1380(w), 1260(w), 1017(s), 612(s), 570(s), 485(m), cm^{-1} ;

terminal carbonyl region (pentane): 2068(s), 2027(vs), 2000(vs), 1997(s), 1981(m) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.47 (t, $J = 7.5\text{Hz}$, 3H, CH_3), 2.62 (m, 2H, SCH_2), 4.32 (AB quartet, 2H, $J_{\text{AB}} = 13.1\text{Hz}$, SCH_2Ph) and 7.30 (m, 5H, Ph).

^{13}C NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 18.7 (q, $J = 129\text{Hz}$, CH_3), 35.8 (t, $J = 142\text{Hz}$, SCH_2), 46.1 (t, $J = 144\text{Hz}$, SCH_2Ph), 128.4 (d,

$J = 154\text{Hz}$, Ph), 129.3 (d, $J = 160\text{Hz}$, Ph), 129.6 (d, $J = 161\text{Hz}$, Ph), 134.3 (s, ipso Ph), 207.7, 210.8, 211.6 (all s, CO) and 304.6 (s, C=S).

Mass spectrum, m/z (relative intensity): 508 (M^+ , 7), 480 ($M^+ - \text{CO}$, 10), 452 ($M^+ - 2\text{CO}$, 5), 424 ($M^+ - 3\text{CO}$, 82), 396 ($M^+ - 4\text{CO}$, 59), 368 ($M^+ - 5\text{CO}$, 39), 340 ($M^+ - 6\text{CO}$, 100), 312 ($\text{Fe}_2\text{S}_3\text{C}_8\text{H}_8$, 96), 249 ($\text{Fe}_2\text{S}_3\text{C}_3\text{H}_5$, 11), 264 ($M^+ - 6\text{CO} - \text{CS}_2$, 31), 236 ($\text{Fe}_2\text{SC}_7\text{H}_8$, 98), 221 ($\text{Fe}_2\text{S}_3\text{CH}$, 73), 176 (Fe_2S_2 , 60), 144 (Fe_2S , 70), 91 (PhCH_2 , 76).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}_3$: C, 37.82; H, 2.38%.

Found: C, 37.99; H, 2.57%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture, Carbon Disulfide and Iodomethane. (GBW-X-16).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 0.5 ml (8.0 mmol) of carbon disulfide (MCB). The mixture was allowed to stir for 1 h prior to the addition of 0.5 ml (8.0 mmol) of iodomethane (Aldrich). Stirring then was continued for 2.5 h during which time the solution became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (9/1, v/v) eluted a red band which gave 1.23 g (2.84 mmol, 96% yield) of $(\mu\text{-MeSCS})-(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red, air-stable solid, mp 77-78°C after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3006(m), 2992(m), 2972(m), 2890(w), 1457(m), 1437(w), 1422(m), 1381(m), 1311(w), 1259(m), 1020(s), 958(m), 612(s), 570(s), 490(m) cm^{-1} ;

terminal carbonyl region (pentane): 2068(s), 2028(vs), 2000(vs), 1997(s), 1982(m) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.46 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 2.54 (s, 3H, SCH_3) and 2.59 (m, 2H, SCH_2).

^{13}C NMR (CDCl_3 , 67.9Hz): δ_{C} 18.3 (q, $J = 128\text{Hz}$, CH_3), 24.1 (q, $J = 140\text{Hz}$, SCH_3), 35.1 (t, $J = 141\text{Hz}$, SCH_2), 207.1, 210.2, 210.8 (all s, CO), 209.6 (broad, CO) and 306.0 (s, $\text{C}=\text{S}$).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{Fe}_2\text{O}_6\text{S}_3$: C, 27.80; H, 1.87%.

Found: C, 28.01; H, 2.24%.

Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Iodomethane. (GBW-IX-51).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this mixture was added 1.0 ml (16.1 mmol) of iodomethane (Aldrich) and the solution was stirred for 24 h. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted two yellow bands which were collected together and gave 0.15 g (0.37 mmol, 13% yield) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ as a red solid identified by comparison of its ^1H NMR spectrum to that of an authentic sample.⁴¹ An isomer ratio of 2/1 (e,a/e,e) was determined by integration of the ^1H NMR spectrum.

Attempted Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Iodomethane at Reflux. (GBW-X-29).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this mixture was added 1.0 ml (16.1 mmol) of iodomethane and the solution was refluxed for 30 min. Stirring was continued an additional 30 min as the solution cooled. Removal of the solvent left a brown oil which was subjected to filtration chromatography (silicic acid/pentane). No tractable products could be eluted from the column.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Methyl Isothiocyanate. (GBW-X-18).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 0.25 ml (3.50 mmol) of methyl isothiocyanate (Aldrich). The mixture was stirred for 30 min prior to the addition of 0.50 ml (8.0 mmol) of iodomethane (Aldrich). Stirring then was continued for 20 h during which time the solution became red. The solvent was removed leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 1.10 g (2.65 mmol, 89% yield) of $(\mu\text{-Me(H)NCS})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red-brown, air-stable solid, mp 127-129°C dec after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3420(s) ν (N-H), 3005(m), 2990(w), 2973(m), 2941(w), 2928(w), 1511(s) ν (C-N), 1457(m), 1437(w), 1380(w), 1357(s), 1256(m), 1160(m), 1000(s), 874(s), 617(s), 580(s), 490(m) cm^{-1} ;

terminal carbonyl region (pentane): 2068(s), 2027(vs), 2000(vs), 1989(s), 1967(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.48 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 2.61 (m, 2H, SCH_2), 3.0 (d, $J = 4.9\text{Hz}$, 3H, NCH_3) and 7.29 (broad, 1H, NH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 18.4 (q, $J = 129\text{Hz}$, CH_3), 35.3 (t, $J = 140\text{Hz}$, SCH_2), 35.5 (q, $J = 139\text{Hz}$, NCH_3), 209.0, 209.4, 213.1 (all s, CO), 210.3 (broad, CO) and 249.7 (s, $\text{C}=\text{S}$).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{Fe}_2\text{O}_6\text{NS}_2$: C, 28.94; H, 2.19%.

Found: C, 28.96; H, 2.23%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Methyl Isocyanate. (GBW-X-23).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 0.25 ml (4.5 mmol) of methyl isocyanate (Aldrich). The mixture then was refluxed for 30 min and stirred an additional 30 min without heating prior to removal of the solvent. A red tar was left which was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The solvent was removed from the red filtrate leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.39 g (0.98 mmol, 33% yield) of $(\mu\text{-Me(H)NCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red, air-stable solid, mp 96-97°C dec after crystallization from pentane/ CH_2Cl_2 .

IR (CH_3Cl_3): 3470(s) (N-H), 2990(w), 2972(m), 2936(m), 2870(w), 1506(s) $\nu(\text{C-N})$, 1480(s) $\nu(\text{C=O})$, 1457(m), 1397(s), 1380(m), 1258(m), 1154(m), 983(m), 612(s), 582(s) cm^{-1} ;

terminal carbonyl region (pentane): 2078(s), 2033(vs), 2003(vs), 1994(vs), 1970(s) cm^{-1} .

^1H NMR (CDCl_3 , 270MHz): δ 1.50 (t, $J = 7.1\text{Hz}$, 3H, CH_2CH_3), 2.55 (d, $J = 4.4\text{Hz}$, 3H, NCH_3), 2.53 (m, 2H, SCH_2) and 5.59 (broad, 1H, NH).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 18.4 (q, $J = 130\text{Hz}$, CH_2CH_3), 28.0 (q, $J = 139\text{Hz}$, NCH_3), 32.6 (t, $J = 144\text{Hz}$, SCH_2), 209.5, 213.8, 214.3 (all s, carbonyl groups).

Mass spectrum, m/z (relative intensity): 399 (M^+ , 15), 371 ($\text{M}^+ - \text{CO}$, 25), 343 ($\text{M}^+ - 2\text{CO}$, 34), 315 ($\text{M}^+ - 3\text{CO}$, 65), 287 ($\text{M}^+ - 4\text{CO}$, 31), 259 ($\text{M}^+ - 5\text{CO}$, 49), 231 ($\text{M}^+ - 6\text{CO}$, 100), 203 ($\text{Fe}_2(\text{SEt})\text{NMeH}$, 97), 188 (Fe_2NSEt , 4), 174 (Fe_2SNMeH , 35), 173 (Fe_2SNME , 58), 145 (Fe_2SH , 78), 144 (Fe_2S , 74), 112 (Fe_2 , 8), 56 (Fe, 29).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{Fe}_2\text{O}_7\text{NS}$: C, 30.11; H, 2.27%.

Found: C, 30.06; H, 2.34%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and Phenylacetylene. (GBW-X-17,20).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325); to this solution was added 0.35 ml (3.19 mmol) of phenylacetylene (Fluka). The solution was stirred for 42 h at room temperature. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band

which was not collected. Elution with pentane/ CH_2Cl_2 (9/1, v/v) moved a red band which gave 0.86 g (1.94 mmol, 65% yield) of 25 and 26 as a red, air-stable solid, mp 80-82°C after crystallization from pentane. An isomer ratio of 2/1 (25/26) was determined from the ^1H NMR spectrum. Spectroscopic measurements were carried out on the 25/26 mixture.

IR (CHCl_3): 2990(w), 2970(m), 2930(m), 2870(w), 1595(w), 1493(m), 1450(m), 1430(w), 1377(m), 1255(m), 1073(w), 1022(w), 967(m), 874(w), 687(m), 636(m), 610(s), 590(s), 522(m), 490(m) cm^{-1} ;

terminal carbonyl region (pentane): 2069(s), 2035(vs), 2000(vs), 1995(vs) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.38 (4 lines, overlapping triplets, $J = 7.4\text{Hz}$, CH_3), 2.41 (q, $J = 7.4\text{Hz}$, CH_2), 2.42 (d, $J = 2.5\text{Hz}$, $=\text{CH}_2$, 26), 3.60 (d, $J = 2.5\text{Hz}$, $=\text{CH}_2$, 26), 4.40 (d, $J = 13.7\text{Hz}$, $=\text{CHPh}$, 25), 7.2 to 7.4 (complex m, Ph) and 8.50 (d, $J = 13.7\text{Hz}$, Fe_2CH , 25).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 17.9 (q, $J = 129\text{Hz}$, CH_3), 33.7 (t, $J = 143\text{Hz}$, SCH_2 , 25), 34.6 (t, $J = 137\text{Hz}$, SCH_2 , 26), 67.1 (dd, $J = 156\text{Hz}$, $J = 162\text{Hz}$, $=\text{CH}_2$, 26), 95.2 (d, $J = 159\text{Hz}$, $=\text{CH}$, 25), 124.6 to 130.7 (Ph), 139.4 (s, ipso Ph, 25), 144.2 (d, $J = 149\text{Hz}$, Fe_2CH , 25), 156.4 (s, ipso Ph, 26), 187.4 (s, Fe_2CPh , 26) and 209.4 (s, CO).

Mass spectrum, m/z (relative intensity): 444 (M^+ , 18), 416 ($\text{M}^+ - \text{CO}$, 17), 388 ($\text{M}^+ - 2\text{CO}$, 18), 360 ($\text{M}^+ - 3\text{CO}$, 28), 332 ($\text{M}^+ - 4\text{CO}$, 16), 304 ($\text{M}^+ - 5\text{CO}$, 38), 276 ($\text{M}^+ - 6\text{CO}$, 100), 248 ($\text{Fe}_2(\text{HC}=\text{CPhH})\text{SH}$,

77), 144 (Fe_2S , 76), 56 (Fe , 25).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}$: C, 43.28; H, 2.72%.

Found: C, 43.35; H, 2.80%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and Phenylacetylene at Room Temperature. (GBW-X-35).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326); to this mixture was added 0.35 ml (3.19 mmol) of phenylacetylene (Fluka). The solution was stirred for 49 h becoming dark red. The solvent was removed leaving a red oil which was taken up in pentane/ CH_2Cl_2 (1/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to filtration chromatography. Pentane eluted a yellow band which gave 0.10 g (0.22 mmol, 7% yield) of $(\mu\text{-Me}_3\text{CS})_2\text{Fe}_2(\text{CO})_6$, a known compound, identified by ^1H NMR.⁴² Continued elution with pentane moved a red band which gave 0.32 g (0.68 mmol, 23% yield) of a mixture of 27 and 28 as an air-stable, red solid, mp 85-90°C after crystallization from pentane. An isomer ratio of 1.6/1 (27/28) was determined from the ^1H NMR spectrum (see page 343).

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and Phenylacetylene at Reflux. (GBW-X-37).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326); to this mixture was added 0.35 ml (3.19 mmol) of phenylacetylene (Fluka). The solution was refluxed for 1 h during which time it became dark red. It then was stirred at room temperature for 4 h prior to removal of the solvent. The

remaining red oil was taken up in pentane/ CH_2Cl_2 (1/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Further elution with pentane moved a red band which gave 0.69 g (1.46 mmol, 49% yield) of 27 and 28 as an air-stable, red solid, mp 85-90°C after crystallization from pentane. An isomer ratio, 27/28 of 1.4/1 was determined from the ^1H NMR spectrum. Spectroscopic measurements were carried out on the 27/28 mixture.

IR (CHCl_3): 2979(m), 2950(m), 2935(m), 2909(w), 2876(w), 1600(w), 1496(w), 1460(m), 1396(w), 1368(m), 1310(w), 1154(m), 1078(w), 1028(w), 692(m), 641(m), 613(s), 596(s), 495(m), cm^{-1} ; terminal carbonyl region (pentane): 2068(s), 2036(vs), 2000(vs), 1993(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.40 (s, t-butyl Me, 27), 1.43 (s, t-butyl Me, 28), 2.79 (d, $J = 2.5\text{Hz}$, $=\text{CH}_2$, 28), 3.58 (d, $J = 2.5\text{Hz}$, $=\text{CH}_2$, 28), 4.68 (d, $J = 13.7$, $=\text{CH}$, 27), 7.20 to 7.30 (m, Ph) and 8.30 (d, $J = 13.7\text{Hz}$, Fe_2CH , 27).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 33.0 (q, $J = 128\text{Hz}$, CH_3 , 27), 33.3 (q, $J = 128\text{Hz}$, CH_3 , 28), 48.1 (s, CMe_3 , 28), 48.3 (s, CMe_3 , 27), 68.8 (dd, $J = 155\text{Hz}$, $J = 163\text{Hz}$, $=\text{CH}_2$, 28), 96.6 (d, $J = 158.0\text{Hz}$, $=\text{CH}$, 27), 124.8 to 130.5 (Ph), 139.3 (s, ipso Ph, 27), 141.5 (d, $J = 145\text{Hz}$, Fe_2CH , 27), 156.9 (s, ipso Ph, 28), 185.0 (s, Fe_2CPh , 28), 208.1, 210.0 and 212.2 (all s, CO).

Mass spectrum, m/z (relative intensity): 472 (M^+ , 6), 444 ($M^+ - CO$, 27), 416 ($M^+ - 2CO$, 9), 388 ($M^+ - 3CO$, 24), 360 ($M^+ - 4CO$, 10), 332 ($M^+ - 5CO$, 19), 304 ($M^+ - 6CO$, 56), 248 ($Fe_2(HC=CPhH)SH$, 100), 144 (Fe_2S , 69), 56 (Fe , 19).

Anal. Calcd. for $C_{18}H_{16}Fe_2O_6S$: C, 45.78; H, 3.42%.

Found: C, 45.69; H, 3.51%.

Reaction Between the Standard $Fe_3(CO)_{12}/Me_3CSH/Et_3N$ Mixture and Acetylene. (GBW-X-39).

The standard $Fe_3(CO)_{12}/Me_3CSH/Et_3N$ reagent solution was prepared (p.326). Acetylene (Farchan) was bubbled into the refluxing solution for 1 h. The mixture was stirred for another hour at room temperature with acetylene bubbling into it. The solvent was removed, leaving a red oil which was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.22 g (0.56 mmol, 20% yield) of $(\mu, \eta^2-H_2C=CH)(\mu-Me_3CS)Fe_2(CO)_6$ as a slightly air-sensitive, red oil.

IR ($CHCl_3$): 2972(s), 2934(s), 2910(m), 2869(m), 1472(m), 1459(s), 1396(w), 1368(s), 1296(m), 1155(s), 1019(w), 984(w), 616(s), 595(s), 499(s) cm^{-1} ;

terminal carbonyl region (pentane): 2068(s), 2035(vs), 2000(vs), 1992(vs) cm^{-1} .

1H NMR (C_6D_6 , 250MHz): δ 1.07 (s, 9H, t-butyl CH_3), 3.08 (d, $J = 13.9Hz$, 1H), 3.35 (d, $J = 9.2Hz$, 1H), 7.77 (dd, $J = 13.9Hz$,

$J = 9.2\text{Hz}$, 1H , Fe_2CH).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 33.0 (q, $J = 126\text{Hz}$, CH_3), 47.8 (s, CMe_3), 74.8 (dd, $J = 163\text{Hz}$, $J = 157\text{Hz}$, $=\text{CH}_2$), 154.8 (d, $J = 151\text{Hz}$, Fe_2CH), 211 to 209 (broad, CO) and 209 (s, CO).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{Fe}_2\text{O}_6\text{S}$: C, 36.40; H, 3.05%.

Found: C, ; H, %.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and Methyl Propiolate. (GBW-XI-11).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326). To this solution was added 0.53 ml (6.0 mmol) of methyl propiolate (Aldrich). An immediate reaction ensued with gas evolution. The solution was stirred 1.5 h and became dark red. Removal of the solvent left a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.66 g (1.45 mmol, 49% yield) of $(\mu, \eta^2\text{-MeO}_2\text{CCH=CH})(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive, red oil.

IR (pentane) terminal carbonyl region: 2080(m), 2052(vs), 2019(s), 2000(vs) and 1728(m) (ester CO).

^1H NMR (CDCl_3 , 250MHz): δ 1.37 (s, 9H, t-butyl CH_3), 3.45 (d, $J = 12.2\text{Hz}$, 1H , CH), 3.70 (s, 3H, OCH_3) and 8.83 (d, $J = 12.2\text{Hz}$, Fe_2CH).

^{13}C (CD_2Cl_2 , 67.9MHz): δ_{C} 33.4 (q, $J = 127\text{Hz}$, t-butyl CH_3), 49.0 (s, CMe_3), 52.1 (q, $J = 144\text{Hz}$, OCH_3), 76.0 (d, $J = 166\text{Hz}$,

$\underline{\text{C}}\text{CO}_2\text{Me}$), 161.3 (d, $J = 154\text{Hz}$, Fe_2CH), 169.7 (s, ester CO) and 208.7 (s, CO).

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{Fe}_2\text{O}_8\text{S}$: C, 37.04; H, 3.11%.

Found: C, 36.57; H, 3.17%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ Mixture and 3-Hexyne. (GBW-X-22).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.325). To this mixture was added 0.41 g (5.0 mmol) of 3-hexyne (Farchan). The solution was stirred for 20 h at room temperature; however, TLC analysis of the mixture showed little product formation. The solution was then refluxed for 20 min prior to removal of the solvent. The remaining red oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted red bands. The first band gave 0.65 g (1.53 mmol, 51%) of $(\mu, \eta^2\text{-EtCH=CEt})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red, air-stable solid, mp 58-60°C after crystallization from pentane.

IR (CHCl_3): 2991(s), 2943(s), 2882(m), 1478(w), 1457(m), 1437(w), 1380(m), 1314(m), 1260(m), 1134(m), 1058(w), 976(m), 871(m), 844(m), 640(m), 620(s), 600(s), 575(s), 500(s) cm^{-1} ;

terminal carbonyl region (pentane): 2079(m), 2068(s), 2036(vs), 1994(vs), 1984(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.14 (t, $J = 7.4\text{Hz}$, CH_3), 1.28 (t, $J = 7.4\text{Hz}$, CH_3), 1.33 (t, $J = 7.4\text{Hz}$, CH_3 of SEt), 1.88, 2.13, 2.40, 2.68 (all multiplets, ethyl CH_2 groups) and 2.84 (t, $J = 6.0\text{Hz}$, vinyl proton).

^{13}C NMR (CDCl_3 , 67.9MHz): δ_{C} 14.7 (q, $J = 131\text{Hz}$, CH_3), 17.9 (q, $J = 128\text{Hz}$, CH_3), 18.6 (q, $J = 131\text{Hz}$, CH_3), 26.2 (t, $J = 128\text{Hz}$, CH_2), 34.2 (t, $J = 141\text{Hz}$, SCH_2), 42.5 (t, $J = 127\text{Hz}$, CH_2), 97.7 (d, $J = 161\text{Hz}$, $=\underline{\text{CH}}$), 183.3 (s, $\text{EtC}\underline{\text{Fe}}_2$), 210.8 (broad, CO).

Mass spectrum, m/z (relative intensity): 424 (M^+ , 22), 396 ($\text{M}^+ - \text{CO}$, 24), 368 ($\text{M}^+ - 2\text{CO}$, 30), 340 ($\text{M}^+ - 3\text{CO}$, 31), 312 ($\text{M}^+ - 4\text{CO}$, 58), 284 ($\text{M}^+ - 5\text{CO}$, 44), 256 ($\text{M}^+ - 6\text{CO}$, 100), 228 ($\text{Fe}_2(\text{EtC}=\text{CH}\text{Et})\text{SH}$, 30), 144 (Fe_2S , 51), 56 (Fe, 5).

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{Fe}_2\text{O}_6\text{S}$: C, 39.66; H, 3.80%.

Found: C, 39.64; H, 3.85%.

The second band gave 0.43 g (0.95 mmol, 32% yield) of $(\text{CO})_3^- (\text{EtCH}=\text{CEt})\text{Fe}(\mu\text{-EtS})\text{Fe}(\text{CO})_4$ as a red, air-stable solid, mp 57-58°C after crystallization from pentane. This material was determined to be a mixture of two isomers in a ratio of 4.5/1 from the integration of the vinyl proton signals in the ^1H NMR spectrum.

IR (CHCl_3): 2980(s), 2940(m), 2880(m), 1629(m) $\nu(\text{C}=\text{C})$, 1454(s), 1442(s), 1379(m), 1320(w), 1258(m), 1074(s), 1058(s), 985(m), 825(s), 610(s), 582(s) cm^{-1} ;

terminal carbonyl region (pentane): 2072(s), 2038(vs), 2031(vs), 1999(vs), 1972(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.61 (t, $J = 7.4\text{Hz}$, CH_3), 1.09 (t, $J = 7.5\text{Hz}$, CH_3), 1.48 (t, $J = 7.4\text{Hz}$, CH_3), 1.80, 2.24, 2.60 (all multiplets, ethyl CH_2 groups), 6.48 (t, $J = 7.4\text{Hz}$, vinyl

proton of major isomer) and 6.65 (t, $J = 7.4\text{Hz}$, vinyl proton of minor isomer).

^{13}C (CDCl_3 , 67.9MHz): δ 13.1 (q, $J = 130\text{Hz}$, CH_3), 13.6 (q, $J = 130\text{Hz}$, CH_3), 18.4 (q, $J = 130\text{Hz}$, CH_3), 19.0 (t, $J = 125\text{Hz}$, CH_2), 22.3 (t, $J = 126\text{Hz}$, CH_2), 32.9 (t, $J = 140\text{Hz}$, SCH_2), 151.2 (s, Fe-C= , minor isomer), 151.7 (s, Fe-C= , major isomer), 153.9 (d, $J = 152\text{Hz}$, $=\text{CH}$, major isomer), 155.5 (d, $J = 156\text{Hz}$, $=\text{CH}$, minor isomer), 206.4, 208.8, 209.6, 209.7, 210.8 and 212.7 (all s, CO).

Mass spectrum, m/z (relative intensity): 452 (M^+ , 20), 424 ($\text{M}^+ - \text{CO}$, 21), 396 ($\text{M}^+ - 2\text{CO}$, 37), 368 ($\text{M}^+ - 3\text{CO}$, 43), 340 ($\text{M}^+ - 4\text{CO}$, 42), 312 ($\text{M}^+ - 5\text{CO}$, 73), 284 ($\text{M}^+ - 6\text{CO}$, 100), 256 ($\text{M}^+ - 7\text{CO}$, 48), 144 (Fe_2S , 40), 56 (Fe, 5).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{Fe}_2\text{O}_7\text{S}$: C, 39.86; H, 3.57%.

Found: C, 39.97; H, 3.61%.

Reaction Between the Standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ Mixture and 3-Hexyne. (GBW-XI-10).

The standard $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ reagent solution was prepared (p.326). To this solution 0.80 g (9.74 mmol) of 3-hexyne (Farchan) was added. The mixture was stirred at reflux for 30 min, then it was stirred at room temperature for 5 h. The solvent was removed leaving a red oil which was taken up in pentane/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was chromatographed using a column (300 x 25 mm) of silicic acid. Pentane eluted three bands. The first yielded

0.47 g (1.04 mmol, 35% yield) of $(\mu, \eta^2\text{-EtCH=CEt})(\mu\text{-Me}_3\text{CS})_2\text{Fe}_2\text{-(CO)}_6$ as a red, air-stable solid, mp 65-67°C after crystallization from ethanol.

IR (CHCl_3): 2978(s), 2940(m), 2909(m), 2880(m), 1475(w), 1460(m), 1398(w), 1369(m), 1313(w), 1157(m), 1133(w), 868(w), 839(w), 620(s), 602(s), 568(s), 499(s) cm^{-1} ;

terminal carbonyl region (pentane): 2063(s), 2029(vs), 1991(vs), 1980(s) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 1.13 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 1.26 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 1.38 (s, 9H, t-butyl), 1.87(br), 2.13(br), 2.61(br), 2.72(br) (4H, CH_2 groups) and 3.19 (t, $J = 6.0\text{Hz}$, vinyl).

^{13}C NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 15.1 (q, $J = 126\text{Hz}$, CH_3), 18.8 (q, $J = 127\text{Hz}$, CH_3), 26.2 (t, $J = 126\text{Hz}$, CH_2), 33.4 (q, $J = 132\text{Hz}$, t-butyl CH_3), 43.4 (t, $J = 128\text{Hz}$, CH_2), 48.7 (s, CMe_3), 100.1 (d, $J = 156\text{Hz}$, CH), 180.8 (s, Fe_2C), 210.7 and 212.9 (both broad, CO).

Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{Fe}_2\text{O}_6\text{S}$: C, 42.51; H, 4.46%.

Found: C, 42.63; H, 4.57%.

The second band eluted from the column with pentane and gave 0.11 g (0.24 mmol, 8% yield) of $(\mu\text{-Me}_3\text{CS})_2\text{Fe}_2(\text{CO})_6$ identified by its ^1H NMR spectrum.^{3c} The third band was eluted from the column using a pentane/ CH_2Cl_2 (9/1, v/v) mixture. Removal of the solvent gave 0.36 g (0.75 mmol, 25% yield) of $(\text{CO})_3\text{-(EtCH=CEt)Fe}(\mu\text{-Me}_3\text{CS})\text{Fe}(\text{CO})_4$ as a slightly air-sensitive, red

oil. This oil was determined to be a 1.2/1 mixture of two isomers based on the integration of the vinyl proton signals in the ^1H NMR spectrum.

IR (CHCl_3): 2979(s), 2940(s), 2908(sh), 2884(s), 1631(m) (C=C), 1450(vs), 1368(s), 1322(w), 1296(w), 1196(w), 1157(s), 1077(s), 1060(s), 1023(w), 989(m), 895(w), 825(s), 687(w), 610(vs), 580(vs) cm^{-1} ;

terminal carbonyl region (pentane): 2080(m), 2038(vs), 2010(s), 1996(vs), 1972(m) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.62 (t, $J = 7.4\text{Hz}$, CH_3 of major isomer), 0.67 (t, $J = 7.5\text{Hz}$, CH_3 of minor isomer), 1.12 (4 lines, overlapping triplets, CH_3), 1.23 (s, t-butyl of minor isomer), 1.50 (s, t-butyl of major isomer), 1.80 (m, CH_2), 2.24 (m, CH_2), 6.51 (t, $J = 7.3\text{Hz}$, vinyl proton of major isomer) and 6.78 (t, $J = 7.5\text{Hz}$, vinyl proton of minor isomer).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 13.0 (q, $J = 126\text{Hz}$, CH_3), 13.7 (q, $J = 128\text{Hz}$, CH_3), 13.8 (q, $J = 128\text{Hz}$, CH_3), 19.1 (t, $J = 129\text{Hz}$, CH_2), 19.2 (t, $J = 129\text{Hz}$, CH_2), 22.4 (t, $J = 131\text{Hz}$, CH_2), 22.5 (t, $J = 131\text{Hz}$, CH_2), 34.2 (q, $J = 126\text{Hz}$, t-butyl CH_3 of major isomer), 34.8 (q, $J = 124\text{Hz}$, t-butyl CH_3 of minor isomer), 47.8 (s, CMe_3), 49.5 (s, CMe_3), 150.8 (s, $\text{Fe}-\text{C}=\text{}$ of minor isomer), 151.8 (s, $\text{Fe}-\text{C}=\text{}$ of major isomer), 154.7 (d, $J = 156\text{Hz}$, $=\text{CH}$ of major isomer), 155.6 (d, $J = 157\text{Hz}$, $=\text{CH}$ of minor isomer), 207.8, 210.3, 211.3, 211.7, 212.6 and 213.6 (all s, CO).

Anal. Calcd. for $C_{17}H_{20}Fe_2O_7S$: C, 42.53; H, 4.20%.

Found: C, 42.44; H, 4.28%.

Reaction Between $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})Fe_2(CO)_6$, One Equivalent of $LiBEt_3H$ and Diphenylchlorophosphine. (GBW-X-68).

A 250 ml, round-bottomed flask containing 0.85 g (2.21 mmol) of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})Fe_2(CO)_6$ was equipped with a stir-bar and a serum cap and flushed with nitrogen. THF (50 ml) was added and the red solution cooled to -78°C ; whereupon, 2.21 ml (2.21 mmol) of a 1.0M $LiBEt_3H$ solution in THF was added by syringe. The solution became brown and was stirred for 30 min. Diphenylchlorophosphine, 0.40 ml, 2.21 mmol, (Strem) was added and the solution removed from the cold bath. The reaction mixture was stirred for 20 h during which time it became dark red. The solvent was removed on a rotary evaporatory leaving a red oil which was extracted with pentane/ CH_2Cl_2 (1/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which then was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (9/1, v/v) eluted an orange band which gave 0.64 g (1.22 mmol, 55% yield) of $(\mu\text{-Ph}_2P)(\mu\text{-EtS})Fe_2(CO)_6$ identified by comparison of its mp and ^{31}P NMR spectrum with that of an authentic sample. A second dark red band was eluted from the column with a 3/1 (v/v) pentane/ CH_2Cl_2 mixture giving 0.41 g (0.70 mmol, 32% yield) of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})Fe_2(CO)_5PPh_2OEt$ as a dark red air-stable oil.

IR ($CHCl_3$): 3067(m), 2990(m), 2935(m), 2904(w), 2873(w), 1688(w),

1674(w), 1502(s) ν (acyl CO), 1482(m), 1451(w), 1432(m), 1390(m), 1378(w), 1342(m), 1308(w), 1258(m), 1184(w), 1156(w), 1106(s), 1097(s), 1031(s), 999(w), 972(w), 935(s), 693(s), 636(m), 610(s), 570(s), 521(s) cm^{-1} ;

terminal carbonyl region (pentane): 2040(vs), 2023(m), 1983(vs), 1958(s), 1939(m) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.23 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 1.33 (t, $J = 7.0\text{Hz}$, 3H, CH_3), 2.16 (m, 2H, SCH_2), 2.19 (s, 3H, acyl CH_3), 3.92 (m, 2H, OCH_2), 7.48 and 7.72 (both m, 10H, Ph).

^{13}C NMR (CD_2Cl_2 , 67.9MHz): δ_{C} 16.7 (q, $J = 128\text{Hz}$, CH_3), 18.2 (q, $J = 128\text{Hz}$, CH_3), 32.0 (t, $J = 140\text{Hz}$, SCH_2), 47.2 (q, $J = 128\text{Hz}$, acyl CH_3), 63.6 (t, $J = 142\text{Hz}$, OCH_2), 127 to 132 (Ph), 138.7 (d, $J(\text{P}-\text{C}) = 48\text{Hz}$, ipso Ph), 210 to 218.5 (FeCO) and 300.3 (s, acyl CO).

^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , 36.2MHz): δ_{P} 153.6(s).

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{Fe}_2\text{O}_7\text{PS}$: C, 47.13; H, 3.96%.

Found: C, 47.49; H, 4.13%.

Reaction Between $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, LiBEt_3H and Allyl Chloride. (GBW-IX-54).

By syringe, 2.0 ml (2.0 mmol) of a 1.0M LiBEt_3H solution (Aldrich) was added to a -78°C , THF (50 ml) solution of 0.38 g (0.99 mmol) of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$. The mixture became brown and was stirred for 20 min prior to addition of 0.50 ml (6.13 mmol) of allyl chloride (Aldrich). The solution immediately became red and was removed from the cold bath and stirred for 2 h. Removal of the solvent left a red oil which was

subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.31 g (0.807 mmol, 82% yield) of $(\mu\text{-CH}_2\text{CHCH}_2)(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an air-stable, red solid, mp 40-42°C after crystallization from methanol. It was identified by comparison of its ^1H NMR spectrum to that of an authentic sample (see page 355).

Reaction Between $(\mu,\eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, LiEt_3BH and Propargyl Bromide. (GBW-IX-56).

By syringe, 2.82 ml (2.82 mmol) of a 1.0M LiEt_3BH solution (Aldrich) was added to a -78°C, THF (50 ml) solution of 0.54 g (1.41 mmol) of $(\mu,\eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$. The mixture became brown and was stirred for 20 min prior to addition of 0.70 ml (9.3 mmol) of propargyl bromide (Aldrich). The solution immediately became red and was removed from the cold bath and stirred for 2 h. Removal of the solvent left a red oil which was taken up in pentane/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.30 g (0.79 mmol, 56% yield) of $(\mu\text{-}\eta^1,\eta^2\text{-H}_2\text{C}=\text{C}=\text{CH})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red air-stable solid, mp 39-41°C after crystallization from methanol.

IR (CHCl_3): 3004(m), 2985(m), 2945(m), 2882(w), 1754(m) $\nu(\text{C}=\text{C})$, 1700(w), 1457(m), 1427(m), 1382(m), 1258(m), 1165(w), 1038(w), 1010(w), 974(w), 897(w), 847(m), 628(s), 612(s), 580(sh), 560(m) cm^{-1} ;

terminal carbonyl region (pentane): 2072(s), 2039(s), 2000(s) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.29 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 2.37 (q, $J = 7.4\text{Hz}$, 2H, SCH_2), 5.30 (d, $J = 4.9\text{Hz}$, 2H, $=\text{CH}_2$) and 7.39 (t, $J = 4.9\text{Hz}$, 1H, Fe_2CH).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 17.7 (q, $J = 129\text{Hz}$, CH_3), 34.7 (t, $J = 142\text{Hz}$, SCH_2), 93.4 (t, $J = 167\text{Hz}$, $=\text{CH}_2$), 114.8 (d, $J = 162\text{Hz}$, Fe_2CH), 176.6 (s, $\text{Fe}-\text{C}=\text{O}$) and 209.6 (s, CO).

Mass spectrum, m/z (relative intensity): 380 (M^+ , 7), 352 (M^+-CO , 26), 324 (M^+-2CO , 45), 296 (M^+-3CO , 25), 268 (M^+-4CO , 27), 240 (M^+-5CO , 24), 212 (M^+-6CO , 86), 184 ($\text{Fe}_2\text{SC}_3\text{H}_4$, 100), 183 ($\text{Fe}_2\text{SC}_3\text{H}_3$, 32), 144 (Fe_2S , 76), 112 (Fe_2 , 7), 56 (Fe, 14).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}$: C, 34.77; H, 2.12%.

Found: C, 34.70; H, 2.30%.

Reaction Between $(\mu-\eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, LiBEt_3H and Diphenylchlorophosphine. (GBW-IX-44).

By syringe, 0.90 ml (0.90 mmol) of a 1.0M LiBEt_3H solution (Aldrich) was added to a -78°C , THF (30 ml) solution of 0.20 g (0.448 mmol) of $(\mu,\eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$. The mixture became brown and was stirred for 30 min prior to the addition of 0.20 ml (1.11 mmol) of Ph_2PCl (Strem). The solution was removed from the cold bath and stirred for 20 h during which time it became red. The solvent was removed and the remaining red oil taken up in a pentane/ CH_2Cl_2 (1/1, v/v) solution and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid). Pentane/ CH_2Cl_2 (4/1, v/v) eluted an orange band which gave 0.20 g (0.38 mmol, 85% yield) of

$(\mu\text{-Ph}_2\text{P})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as an orange solid, mp 111-112°C after crystallization from pentane/ CH_2Cl_2 .

IR (CHCl_3): 3077(w), 3059(w), 3000(w), 2984(w), 2966(w), 1482(m), 1454(w), 1436(m), 1381(w), 1332(w), 1307(w), 1257(m), 1189(w), 1103(m), 1096(m), 1085(w), 1031(w), 1006(w), 975(w), 699(s), 616(s), 584(s), 523(m) cm^{-1} ;

terminal carbonyl region (pentane): 2063(s), 2025(s), 1990(s), 1980(s), 1970(m), 1943(w) cm^{-1} .

^1H NMR (CD_2Cl_2 , 250MHz): δ 1.32 (t, $J = 7.3\text{Hz}$, 3H, CH_3), 2.54 (dq, $J = 7.3\text{Hz}$, $J(\text{P-H}) = 1.5\text{Hz}$, 2H, CH_2) and 7.2 to 7.7 (m, 10H, Ph).

^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , 36.2MHz): δ_{P} 142.9(s).

Mass spectrum, m/z (relative intensity): 526 (M^+ , 17), 498 ($\text{M}^+ - \text{CO}$, 11), 470 ($\text{M}^+ - 2\text{CO}$, 11), 442 ($\text{M}^+ - 3\text{CO}$, 11), 414 ($\text{M}^+ - 4\text{CO}$, 6), 386 ($\text{M}^+ - 5\text{CO}$, 73), 358 ($\text{M}^+ - 6\text{CO}$, 100), 330 ($\text{Fe}_2\text{PPh}_2\text{SH}$, 84), 252 (Fe_2PPhS , 28), 175 (Fe_2PS , 39), 144 (Fe_2S , 39), 119 (FePS , 28), 112 (Fe_2 , 11), 56 (Fe, 6).

Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{Fe}_2\text{O}_6\text{PS}$: C, 45.66; H, 2.87%.

Found: C, 45.75; H, 2.93%.

Reaction Between $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, LiEt_3H and Allyl Chloride. (GBW-IX-46).

By syringe, 0.90 ml (0.90 mmol) of a 1.0M LiEt_3H solution (Aldrich) was added to a -78°C , THF (30 ml) solution of 0.20 g (0.448 mmol) of $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$. The mixture became brown and was stirred for 30 min prior to addition of 0.50 ml

(6.13 mmol) of allyl chloride (Aldrich). The solution immediately became red and was removed from the cold bath and stirred for 1 h. Removal of the solvent left a red oil which was taken up in pentane/ CH_2Cl_2 (9/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.14 g (0.366 mmol, 82% yield) of $(\mu\text{-CH}_2\text{CHCH}_2)(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a red air-stable solid, mp 40-42°C after recrystallization from methanol.

IR (CHCl_3): 3000(w), 2979(w), 2940(m), 1495(m), 1454(m), 1378(m), 1210(m), 1153(m), 867(w), 623(s), 599(s), 512(m) cm^{-1} ;
terminal carbonyl region (pentane): 2060(s), 2022(s), 1984(vs) cm^{-1} .

^1H NMR (CDCl_3 , 250MHz): δ 0.47 (d, $J = 12.6\text{Hz}$, 2H, FeCH_2 anti), 1.29 (t, $J = 7.4\text{Hz}$, 3H, CH_3), 1.97 (d, $J = 7.5\text{Hz}$, 2H, FeCH_2 syn), 2.47 (q, $J = 7.4\text{Hz}$, 2H, SCH_2) and 4.76 (m, 1H, CH).

^{13}C NMR (C_6D_6 , 67.9MHz): δ_{C} 18.1 (q, $J = 130\text{Hz}$, CH_3), 20.9 (t, $J = 154\text{Hz}$, Fe-CH_2), 32.7 (t, $J = 141\text{Hz}$, SCH_2), 88.5 (d, $J = 158\text{Hz}$, CH) and 211.2 (s, CO).

Mass spectrum, m/z (relative intensity): 382 (M^+ , 5), 354 ($\text{M}^+ - \text{CO}$, 6), 326 ($\text{M}^+ - 2\text{CO}$, 36), 298 ($\text{M}^+ - 3\text{CO}$, 11), 270 ($\text{M}^+ - 4\text{CO}$, 19), 242 ($\text{M}^+ - 5\text{CO}$, 22), 214 ($\text{M}^+ - 6\text{CO}$, 67), 186 ($\text{Fe}_2\text{SC}_3\text{H}_6$, 70), 144 (Fe_2S , 100), 56 (Fe, 29).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Fe}_2\text{O}_6\text{S}$: C, 34.59; H, 2.64%.

Found: C, 34.65; H, 2.74%.

Reaction Between $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$, LiBEt_3H and warming to Room Temperature Prior to the Addition of Diphenylchlorophosphine. (GBW-IX-45).

By syringe, 0.95 ml (0.95 mmol) of a 1.0M LiBEt_3H solution (Aldrich) was added to a -78°C THF (30 ml) solution of 0.21 g (0.47 mmol) of $(\mu, \eta^2\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$. The mixture became brown and was removed from the cold bath and stirred for one hour during which time it warmed up to room temperature. Diphenylchlorophosphine, 0.20 ml (1.11 mmol), was added and the solution stirred for 21 h. The solution remained brown. Removal of the solvent left a brown oil which was taken up in a 1/1 (v/v) CH_2Cl_2 /pentane solution and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane/ CH_2Cl_2 (4/1, v/v) eluted a yellow band which gave 0.081 g (0.154 mmol, 33% yield) of $(\mu\text{-Ph}_2\text{P})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ identified by comparison of its ^{31}P NMR spectra to that of an authentic sample (see page 354).

References

1. Hieber, W.; Spacu, P. Z. Anorg. Allg. Chem. 1937, 233, 353.
2. Kettle, S.F.A.; Orgel, L.E. J. Chem. Soc. 1960, 3890.
3. a) Hieber, W.; Scharfenberg, C. Chem. Ber. 1940, 73, 1012.
b) Manuel, T.A.; Meyer, T.J. Inorg. Chem. 1964, 3, 1049.
c) De Beer, J.A.; Haines, R.J. J. Organomet. Chem. 1970, 24, 757.
d) Nametkin, N.S.; Tyuvin, V.D.; Kukina, M.A. J. Organomet. Chem. 1978, 149, 355.
4. Winter, A.; Zsolnai, L.; Huttner, G. Z. Naturforsch. 1982, 37b, 1430.
5. a) Winter, A.; Zsolnai, L.; Huttner, G. Chem. Ber. 1982, 1286.
b) Bau, R.; Don, B.; Greatrex, R.; Haines, R.J.; Love, R.A.; Wilson, R.D. Inorg. Chem. 1975, 14, 3021.
6. a) Huttner, G.; Zsolnai, L.; Winter, A. J. Organomet. Chem. 1983, 250, 409.
b) Winter, A.; Zsolnai, L.; Huttner, G. J. Organomet. Chem. 1982, 234, 337.
c) Winter, A.; Zsolnai, L.; Huttner, G. J. Organomet. Chem. 1982, 232, 47.
7. Takács, J.; Markó, L. J. Organomet. Chem. 1983, 247, 223.
8. a) Mathey, F.; Comarmond, M.-B.; Moras, D. J. Chem. Soc., Chem. Comm. 1979, 417.

- b) Job, B.E.; McLean, R.A.N.; Thompson, D.T. J. Chem. Soc., Chem. Comm. 1966, 1895.
9. King, R.B.; Treichel, P.M.; Stone, F.G.A. J. Am. Chem. Soc. 1961, 83, 3600.
10. Patin, H.; Mignami, G.; Mahé, C.; Le Marouille, J.-Y.; Southern, T.G.; Benoit, A.; Grandjean, P. J. Organomet. Chem. 1980, 197, 315.
11. Patin, H.; Mignami, G.; Benoit, A.; Le Marouille, J.-Y.; Grandjean, D. Inorg. Chem. 1981, 20, 4351.
12. Womack, G.B. unpublished results, see Chapter 3.
13. Hoke, J.B. unpublished results.
14. Seyferth, D.; Henderson, R.S. J. Organomet. Chem. 1981, 218, C34.
15. Dahl, L.F.; Wei, C.-H. Inorg. Chem. 1963, 2, 328.
16. a) Lourdichi, M.; Mathieu, R. Nouv. J. Chim. 1982, 6, 231.
b) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. J. Am. Chem. Soc. 1983, 105, 4826.
17. Collman, J.P.; Rothrock, R.K.; Finke, R.G.; Moore, E.J.; Rose-Munch, F. Inorg. Chem. 1982, 21, 146.
18. Werner, H.; Kühn, A.; Tune, D.J. Chem. Ber. 1977, 110, 1763.
19. Kobayashi, Y.; Iitaka, Y.; Yamazaka, H. Acta Cryst. B 1972, 28, 899.
20. Werner, H. Adv. Organomet. Chem. 1981, 19, 155.
21. Aokio, T.; Furusaki, A.; Tomiie, Y.; Ono, K.; Tanaka, K. Bull. Chem. Soc. Jap. 1969, 42, 545.

22. a) McDonald, W.S.; Mann, B.E.; Raper, G.; Shaw, B.L.; Shaw, G. J. Chem. Soc., Chem. Comm. 1969, 1254.
b) Raper, G.; McDonald, W.S. J. Chem. Soc., Chem. Comm. 1970, 655.
23. MacGillavry, C.M.; Rieck, G.D. (ed.) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham England, 1974; Vol. III, p. 276.
24. Smith, W.F.; Yule, J.; Taylor, N.J.; Paik, H.N.; Carty, A.J. Inorg. Chem. 1977, 16, 1593.
25. a) Burch, R.R.; Shusterman, A.J.; Muetterties, E.L.; Teller, R.G.; Williams, J.M. J. Am. Chem. Soc. 1983, 105, 3546.
b) Fryzuk, M.D.; Jones, T.; Einstein, F.W.B. Organometallics 1984, 3, 185.
c) Nubel, P.O.; Brown, T.L. J. Am. Chem. Soc. 1984, 106, 3474.
26. a) Shapley, J.R.; Richter, S.I.; Tachikawa, M.; Keister, J.B. J. Organomet. Chem. 1975, 94, C43.
b) Clauss, A.D.; Tachikawa, M.; Shapley, J.R.; Pierpont, C.G. Inorg. Chem. 1981, 20, 1528.
27. a) Hoffmann, K.; Weiss, E. J. Organomet. Chem. 1977, 128, 225.
b) Kruger, C.; Tsay, Y.H.; Grevels, F.W.; Koerner von Gustorf, E. Isr. J. Chem. 1972, 10, 201.
28. ΔG^\ddagger was calculated using the equation
$$\Delta G^\ddagger = 19.14 T_C (9.97 + \log \frac{T_C}{\delta v}) \text{ (J mol}^{-1}\text{)}$$
where T_C is the coalescence temperature (220K) and δv

- the shift difference (Hz) of the two exchange sites in the limiting low temperature spectra. see; Gunther, H. "NMR Spectroscopy, An Introduction"; John Wiley: New York, 1973, p. 243.
29. Nubel, P.O.; Brown, T.L. Organometallics 1984, 3, 29.
30. Jensen, C.M.; Chen, Y.J.; Kaesz, H.D. J. Am. Chem. Soc. 1984, 106, 4046.
31. Yu, Y.-F.; Gallucci, J.; Wojcicki, A. J. Chem. Soc., Chem. Comm. 1984, 653.
32. a) Gibson, J.A.E.; Cowie, M. Organometallics 1984, 3, 722.
- b) Gal, A.W.; Ambrosius, H.P.M.M.; Van Der Ploeg, A.F.M.J.; Bosman, W.P. J. Organomet. Chem. 1978, 149, 81.
33. Grevels, F.-W.; Schulz, D.; Koerner von Gustorf, E.; Bunbury, D.St. P. J. Organomet. Chem. 1975, 91, 341.
34. a) Longato, B.; Norton, J.R.; Huffmann, J.C.; Marsella, J.A.; Caulton, K.G. J. Am. Chem. Soc. 1981, 103, 209.
- b) Jensen, C.M.; Kaesz, H.D. J. Am. Chem. Soc. 1983, 105, 6969.
- c) Rosen, R.P.; Hoke, J.B.; Whittle, R.R.; Geoffroy, G.L.; Hutchinson, J.P.; Zubieta, J.A. Organometallics 1984, 3, 846 and references therein.
35. a) Carmona, E.; Sanchez, L.; Mavin, J.M.; Poveda, M.L.; Atwood, J.L.; Priester, R.D.; Rogers, R.D. J. Am. Chem. Soc. 1984, 106, 3214.
- b) Theopold, K.H.; Becker, P.N.; Bergman, R.G. Ibid. 1982, 104, 5250.

- c) Baird, G.J.; Bandy, J.A.; Davies, S.G.; Prout, K.
J. Chem. Soc., Chem. Comm. 1983, 1202.
- d) Lenhert, P.G.; Lukehart, C.M.; Srinivasan, K. J. Am. Chem. Soc. 1984, 106, 124.
- e) Lukehart, C.M.; Srinivasan, K. Organometallics 1983, 2, 1640.
- f) Liebeskind, L.S.; Welker, M.E. Ibid. 1983, 2, 194.
- g) Liebeskind, L.S.; Welker, M.E.; Goedken, V. J. Am. Chem. Soc. 1984, 106, 441.
- h) Brookhart, M.; Timmers, D.; Tucker, J.R.; Williams, G.D.; Husk, G.R.; Brunner, H.; Hammer, B. Ibid. 1983, 105, 6721.
- i) Buhro, W.E.; Wong, A.; Merrifield, J.H.; Lin, G.Y.; Constable, A.C.; Gladysz, J.A. Organometallics 1983, 2, 1852.
- 36. Dötz, K.H. in "Transition Metal Carbene Complexes"; Verlag Chemie: Weinheim, 1983, pp 198-203.
- 37. a) Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J.-Y.; Grandjean, D. Inorg. Chem. 1981, 20, 4351.
b) Patin, H.; Mignani, G.; Benoit, A.; McGlinchey, M.J.
J. Chem. Soc., Dalton Trans. 1981, 1278.
- 38. Brandsma, L.; Verkruijsse "Synthesis of Acetylenes, Allenes and Cumulenes, A Laboratory Manual"; Elsevier: New York, 1981, p 219.
- 39. See reference 38, p 221.
- 40. McFarlane, W.; Wilkinson, G. Inorg. Syn. 1966, 8, 181.
- 41. Seyferth, D.; Henderson, R.S.; Song, L.-C. Organometallics 1982, 1, 125.

42. Silverman, L.D.; Dewan, J.C.; Giandomenis, C.M.; Lippard, S.J. Inorg. Chem. 1980, 19, 3379.

Biographical Sketch

The author was born on November 23, 1957 in Mountain Home, Idaho, the first child of Samuel B. and Christina M. Womack. His father, a sergeant in the Air Force, traveled much and as a result the author spent much of his childhood in Minnesota, England, Oklahoma and California. Receiving his high school diploma in 1976 from Franklin High School, Franklin, North Carolina, he enrolled at Western Carolina University, but later transferred to the University of North Carolina at Greensboro his sophomore year. In May 1980 he received the Bachelor of Science degree in chemistry and in September of the same year started his graduate education at the Massachusetts Institute of Technology. His thesis research was conducted in the laboratories of Professor Dietmar Seyferth and culminated in September of 1984 with completion of the requirements for the Doctor of Philosophy degree. During his stay at M.I.T., he married Cathie Anne Sebastynowicz on July 17, 1983. The author has accepted a position with Westvaco as a research chemist at their facilities in North Charleston, South Carolina.

Acknowledgments

The author would like to express his gratitude to the following people:

Dietmar Seyferth for his help and encouragement in developing this work.

Cathie, my wife, for her love and for putting up with the late nights and dull weekends I spent writing this "monster".

My parents for always being a source of encouragement and understanding during my graduate career.

My "new" family in Maynard for alot of good meals, good company and support.

Debbie Totten for doing a beautiful job of typing this thesis (I know it was not easy).

John Dewan for performing the X-ray diffraction studies reported in Chapter 4.

All the members of the Seyferth research team past and present who made the MIT experience not only educational but a great deal of fun too.